Progress Report (3rd quarter)

Advanced Lubrication for Energy Efficiency, Durability and Lower Maintenance Costs of Advanced Naval Components and Systems

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Abstract

In boundary lubrication, spacing of mating surfaces in direct physical contact is in the scale of surface asperities. These conditions may benefit from the nanoscale dimension of the advanced nanoparticle lubricants in the following ways: (1) by supplying nano to sub-micron size lubricating agents which reduce friction and wear at the asperity contact zone, (2) by enabling strong metal adsorption and easy wetting, (3) by reacting with the surface to form durable lubricating “transient transfer” films, sustain high loads and also remain under high temperatures, and (4) by enabling all these at minimal cost and great environmental safety. These materials specifically designed on antiwear and extreme pressure chemistries can significantly lower the sulfur and phosphorus level in the lubricant additive and therefore provide environmental benefits.

The project encompasses a detailed investigation of advanced nanolubricants (NanoGlide®) that favorably impact robust boundary film formation to reduce wear and friction. These active nanolubricant additives are designed as surface-stabilized nanomaterials that are dispersed in a hydrocarbon medium for maximum effectiveness. This effort is focused on developing active nanoparticle composites, optimizing process design, physical and chemical characterization of nanomaterials, detailed tribological film characterization, and tribological testing to document friction and wear improvements.

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Summary

In this project we are developing extreme-pressure additives based on surface modified nano molybdenum sulfide (MoS_2). These additives are based on "green" surface chemistries and will have application in the many heavy duty lubrication systems used by the Navy, imparting lower friction, higher reliability, and longer life, leading to reduced energy usage and increased mission availability. They will also have potential for use throughout commercial industries.

In the third quarter of this project, two initial formulations of NanoGlide were modified to specifically address their application as additives in gear oils and greases. These improved formulations were investigated through chemical, structural, and tribological analysis. A Design of Experiments (DoE) approach for synthesis and optimization using scaled up production equipment was applied to analyze interaction between process parameters and to select optimal synthesis parameters to be used with optimal process time.

Tribological testing of NanoGlide® additives in gear oils using Pin-on-Disk test and Block-on-Ring test, and in greases using 4 Ball test and EP 4 Ball test was performed. An evaluation and comparison of their performance is presented and discussed in this report. Equipment that will be used for FZG testing is being prepared now and is on schedule to support FZG tests that will test the NanoGlide formulations with actual gears using a standard test protocol.

This project has revealed several advantages of having NanoGlide® in lubricant formulations (gear oils and greases). It provides advanced lubrication for severe friction conditions (extreme pressure and loads) by extending component life and lube-drain intervals in comparison with base oils and greases. It is a technology that could increase the efficiency and durability of machinery components particularly gears, leading to longer operation intervals and lower maintenance costs. Another beneficial feature is that it is non-disruptive and insertable into current lubricant production processes, and there is a wide range of industrial applications in which it can be put to use with similar advantages.

The scaled-up production process was developed and process parameters were optimized. Morphological and tribological properties of samples from larger-scale production were compared with properties of samples from laboratory-scale production.

This comparison demonstrated the ability to achieve a similar particle size distribution without any significant increase in the level of agglomeration of nanoparticles, and a shortened process time for the scaled-up production process. This contributes to the technical objective of extended shelf life and suspension stability of the nanoparticle additives, and to the commercial goal of increasing yield per batch with significant reduction of the processing time.

The project is on track.

Introduction

This project focuses on research and development of active family of nanolubricant additives, called NanoGlide®, for applications in the US Navy. In previous work, NanoMech has explored the fundamental science of nanoparticle design and synthesis using a top-down nanomanufacturing process, including the mechanisms of synthesis, interaction of “simple organic and inorganic materials” for deagglomerated nanostructures, dispersion stability, and preliminary tribological behavior, and promising results have been observed that give a solid foundation for realistic and valuable application-specific product development [1, 2]. Now the challenge is to experiment further with this concept to apply the underlying science in investigating the feasibility of NanoGlide application for preferred and versatile materials that are of importance to the Navy and currently used in the lubricant industry.

The findings from NanoMech’s preliminary studies are of significant importance in the development of active nanoparticle-based lubricants for mechanical parts and devices, showing outstanding lubrication properties under extreme pressure (EP) and related transient high temperature conditions where boundary layer lubrication is crucial [3], using an environmentally acceptable chemistry..

Devices for energy transfer such as gears, pins, shafts and others inevitably involve mechanical motion, which in turn entails varying degrees of contact and interaction between different types of surfaces, often under environments of extreme-pressure and high-load bearing stresses. An unavoidable consequence of contact between moving surfaces is a force resisting this relative motion - friction. There are two aspects that warrant special attention in this regard; first, mechanical applications are rapidly advancing in a direction that requires machinery to operate at higher loads, speeds and temperatures and often in extremely hostile conditions; and second, greater savings in cost and materials can be achieved through improved lubrication.

To combat the harmful effects of wear and friction, contact surfaces are provided with lubrication. Most lubricants nowadays incorporate one or more additives in order to enhance specific chemical or physical properties. The action of such additives is required when high loads or low speeds disrupt or fail to maintain the hydrodynamic film and boundary lubrication is ushered in. Under boundary lubrication conditions, asperities are no longer separated by a lubricant film and are forced to engage non-elastically. The lubricant additives step in to form a film that forestalls adhesion and lowers wear rate considerably. One such additive that has shown significant promise based on early feasibility testing is NanoGlide®, a multicomponent colloidal lubricant additive that can perform multiple functions, offering extreme pressure lubrication, reduction in the coefficient of friction, and reduced wear under boundary lubrication conditions. The goal in developing NanoGlide was to provide a platform for producing additive systems for lubricants that will (1) reduce wear, lower friction and improve efficiency and durability of equipment, (2) minimize sulfur and phosphorus content and also lower ash forming elements, and (3) provide an advanced lubrication technology that is friendlier to the environment.

Project Objectives

The high-level objective of this project is to develop nanoparticle-based additives to improve friction and wear characteristics of naval components and systems with a focus to enhance durability and energy efficiency, reduce maintenance costs, and improve environmental sustainability.

For this project, NanoMech is performing following technical tasks that are based on the overall project research plan (see Appendix, Table A1):

1. Design of application-specific active nanolubricants (NanoGlide®);
2. Process scale-up and nanomanufacturing of NanoGlide®;
3. Synthesis, de-agglomeration, and optimization of NanoGlide®;
4. Structural, chemical, and physical analysis of NanoGlide®;
5. Tribological testing of NanoGlide®;
6. Commercialization of NanoGlide®.

Project Scope

In the third project quarter, the developed formulations (see first and second quarter reports) were compared to distinguish the effects of these unique additives in providing reduced friction and wear and evaluate their tribological performance. The best-performing candidates were selected and characterized using a number of analytical techniques.

The Design of Experiments approach was used for parameter optimization and scale-up of the process used to synthesize multi-component nanoparticle additive systems for oils and greases. Extensive laboratory-based tribological evaluation of nanomaterials was performed to evaluate friction and wear characteristics in the boundary lubrication regime using Block-on-Ring, Pin-on-Disc, 4 Ball and Extreme Pressure 4 Ball tests. Following this laboratory tribological testing, the performance of the NanoGlide additives will be evaluated in military certified oils using Wedeven Associates' WAM Scuffing Load Capacity Tests in the next project quarter.

Physical and chemical characterization of the additives was performed using a range of microscopic and surface analytic tools (TEM, EDX, XRD, and SEM). The focus was on understanding the inorganic-organic interface chemical behavior resulting in surface lubrication, dispersion of the additives in the hydrocarbon media, and formation of tribofilms at the friction points. Specimens from tribotesting were collected and used for tribofilm analysis using XPS, Auger, and TOF-SIMS. The analysis was carried out in part in the Physics Department and Materials and Manufacturing Research Laboratories (University of Arkansas in Fayetteville) and in the Frederick Seitz Materials Research Laboratory Central Facilities (University of Illinois in Urbana-Champaign) which are partially supported by the U.S. Department of Energy under grants DE-FG02- 07ER46453 and DE-FG02-07ER46471.

Major Activities

The research activities as outlined in the project plan (3rd quarter, Table A1) for the funding phase May 20, 2010 – August 19, 2010 are noted below. The major activities of the project team during this reporting period were:

Task 1. ***Designing of application-specific active nanolubricant (NanoGlide)*** (*Timeline for Task 1: November 2009 – August 2010*);

Task 2. ***Process scale up and nanomanufacturing of NanoGlide*** (*Timeline for Task 2: January – August 2010*);

Task 3. ***Synthesis, de-agglomeration and optimization of NanoGlide*** (*Timeline for Task 3: January – August 2010*);

Task 4. Structural, chemical and physical analysis of NanoGlide (*Timeline for Task 4: March – October 2010*);

Task 5. Tribological testing of NanoGlide (*Timeline for Task 5: March – October 2010*).

Task 6. Commercialization of NanoGlide (*Timeline for Task 6: May – November 2010*).

Specific tasks with timeline for deliverables and milestones to be performed by NanoMech including tasks for the University of Arkansas as a subcontractor and their progress are described below.

Task 1: Designing of application-specific active nanolubricant (NanoGlide®)

(*Timeline for Task 1: November 2009 – August 2010*)

In this task, the project team has already designed the application-specific active nanolubricant that contains inorganic nanoparticles integrated with organic molecular medium to add additional lubrication properties and form protective capping layer to suspend them in base oil medium and protect from sedimentation.

The open-ended ellipsoidal architecture of the nanoparticles prepared by lab scale mill, as seen from the images below (Figure 1), provides for inter-planar slippage, exfoliation and ability to supply reactive transfer films on the mating surfaces, thus protecting the underlying substrate from wear and seizure. Nanoparticles form the inorganic core/carrier integrated with phosphorus-based compounds or environmentally benign vegetable oil/phospholipid molecules in a stable surface stabilized composition.

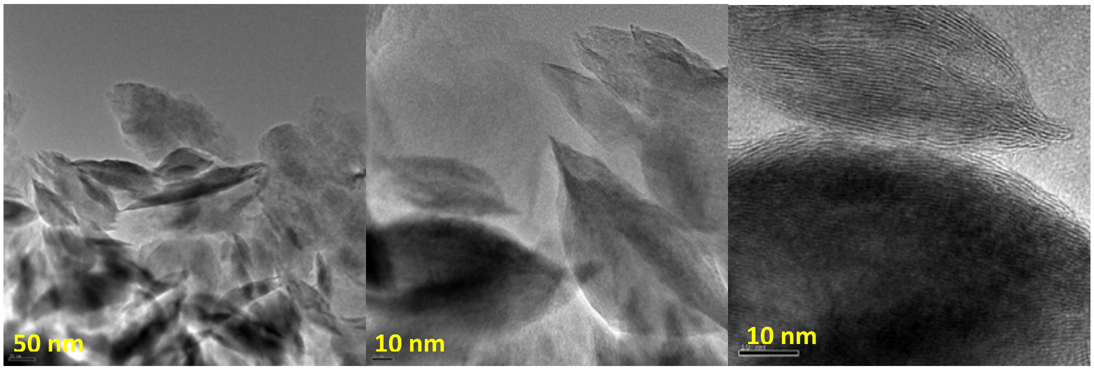

Figure 1. HRTEM images of NanoGlide

The initially prepared two formulations based on nanoparticles with a capping layer of EP additive and/or vegetable oil and dispersant (see 2nd quarter report) were evaluated for lubrication applications (additives to gear and motor oils and greases) and were used as a base for formulation modification and improvement. In the 3rd quarter, modified formulations were prepared in the same way as the initial formulations, but additional chemistries were added during chemo-mechanical milling to increase their lubrication performance and address specific applications in gear oils and greases. The modified nanolubricants were characterized and compared with the two initially prepared formulations. For details on the observed morphological properties of the modified formulations see Task 4 of this report, and for a comparison of their tribological performance please see Task 5 of this report.

<u>Deliverables</u>

Accomplished deliverables:

1. Design of application-specific active nanolubricants of interest to the Navy and potential Navy customers/collaborators;
2. Materials for synthesis of nanoparticles selected for application as additives in gear oils and greases;
3. Synthesis and optimization of the developed nanolubricant formulations at the lab scale;
4. Structural, chemical, and physical analysis of the developed nanolubricant formulations (see Task 4 for more details).

Task 2: Process scale up and nanomanufacturing of NanoGlide®

(*Timeline for Task 2: January – August 2010*)

The process scale up was one of the major tasks explored for this project period. The objectives of scaling-up the nanolubricant production process are to obtain higher process yield by moving to a pilot scale industrial process, achieve cost targets that are commercially viable, and develop protocols for safe handling of the active Extreme Pressure –Environmentally Acceptable (EP-EA) material in quantities approaching a commercial scale.

Both the laboratory bench and pilot scale production mills were used to produce the same nanolubricant formulation. The mills perform particle size reduction and chemo-mechanical milling within a surrounding medium of as organic molecules. The Design of Experiment (DoE) approach was used to optimize the scaled-up processing to achieve the technical objectives of (1) obtaining similar morphological properties between samples prepared with the scaled-up (pilot-scale) process and those synthesized in the laboratory-scale process, and (2) determining the optimal milling parameters for the pilot-scale mill processing. Additional quality-related objectives during synthesis and optimization included: 1) reduction of synthesis time, 2) predictability in particle size, 3) nanoparticle capping consistency, and 4) avoiding agglomeration of nanoparticles.

The particle size of each run of milled sample was analyzed by use of a particle size analyzer, and the particle morphology was analyzed using SEM and/or TEM. Results were compared based on particle size differences and level of agglomeration.

The nanoparticle samples were collected for variable parameters following the DOE matrix and were used for optimization of NanoGlide® synthesis and scale-up (Table 1). The optimization of parameters for chemo-mechanical milling (milling media fraction, media-material ratio, and milling speed) was based on the evaluation of nanoparticles characterized by Particle Size Analysis (mean particle size by number and volume), X-Ray Diffraction Spectroscopy (crystallite sizes from half-width peak in XRD pattern), and shape and agglomeration rate from Transmission Electron Microscopy.

Table 1. Design of Experiments Matrix

Media Fraction	Media-Material Fraction	RPM	Mean Particle Size (number)	Mean Particle Size (volume)	XRD FWHM	TEM size/shape (1-10)
1	A	C	366 nm	3.346 um	0.2125	8
0	C	A	380 nm	1.585 um	0.3244	1
1	C	A	347 nm	1.787 um	0.4214	5
0	C	A	375 nm	3.035 um	0.2077	9
0	A	C	513 nm	1.941 um	0.268	2
0.5	B	B	330 nm	1.960 um	0.2575	3
1	C	A	380 nm	2.320 um	0.2321	4
0	A	C	477 nm	4.309 um	0.1999	7
1	A	C	314 nm	2.610 um	0.2704	6

Analysis of the nanoparticle crystallites (based on half peaks length measurements) showed that the size of crystallites was strongly dependent on speed of milling media rotation in chemo-mechanical milling (Figure 2).

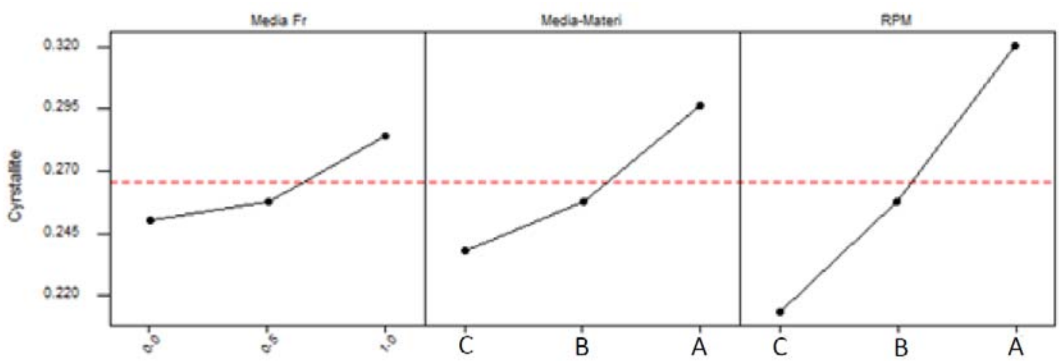

Figure 2. Crystallite vs. Media fraction, Media-Material ratio, and RPM

The analysis of particle size distribution (by number (Figure 3) and volume (Figure 4)) confirmed the competition of two processes during chemo-mechanical milling. The leading fracturing process of bulk particles gives the smallest nanoparticle sizes, while the agglomeration process takes over to form larger secondary particles (agglomerates). The selection of milling media fraction plays important role in achieving the smallest particle sizes. Milling speeds were shown to impact the rates of particle agglomeration.

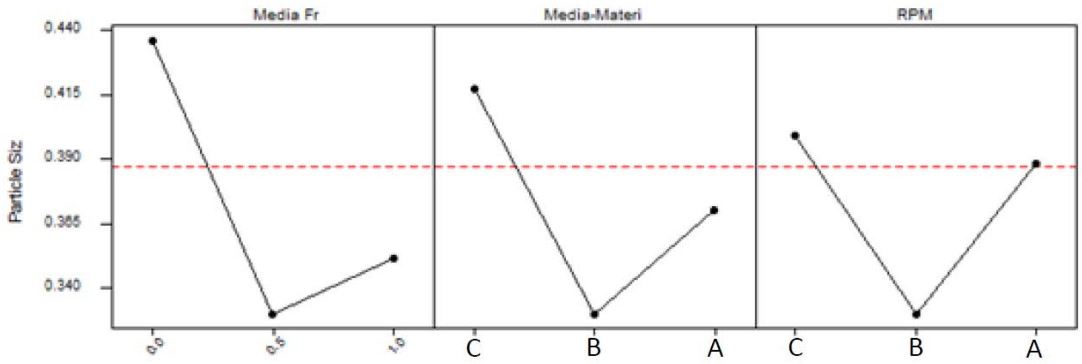

Figure 3. Particle size by number vs. Media fraction, Media-Material ratio, and RPM

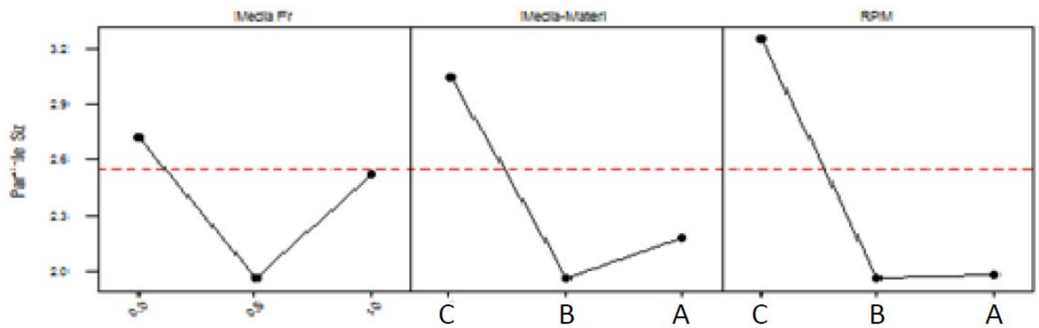

Figure 4. Particle size by volume vs. Media fraction, Media-Material ratio, and RPM

The comparison of shape/size of nanoparticles was based on the ranking of TEM images of prepared samples (scale 1 to 10). The main consideration in ranking was for to achieve samples with particles having uniform dispersion of shape and size and a low rate of agglomeration (Figure 5).

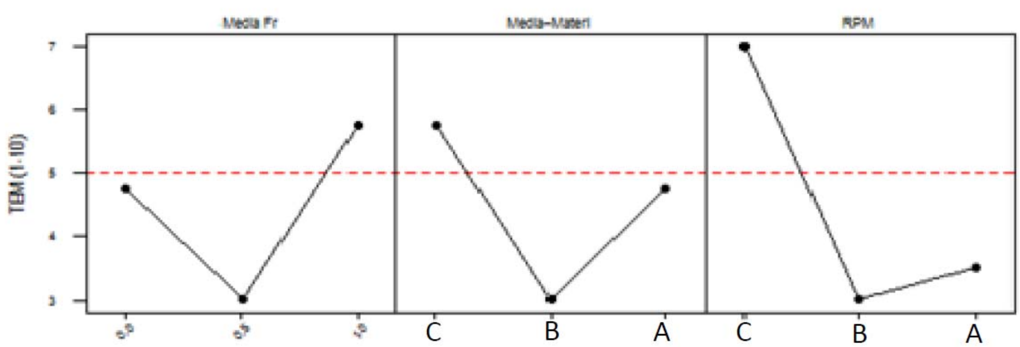

Figure 5. TEM size/shape vs. Media fraction, Media-Material ratio, and RPM

The interaction plots (Figures 6-9) of selected parameters helped to understand interactions between these parameters for the chemo-mechanical process to produce nanoparticles for NanoGlide.

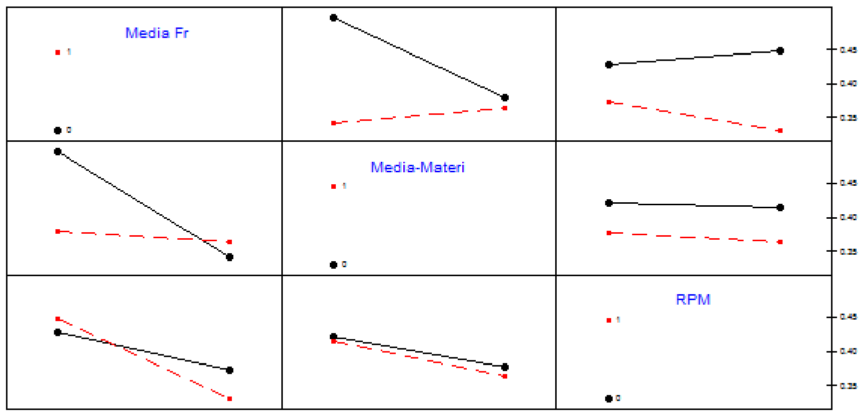

Figure 6. Interaction plot Particle Size by number vs. Media fraction, Media-Material ratio, and RPM

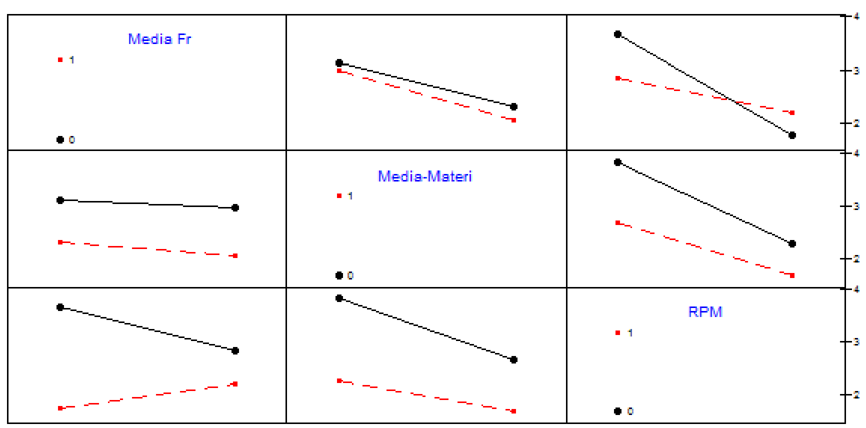

Figure 7. Interaction plot Particle Size by volume vs. Media fraction, Media-Material ratio, and RPM

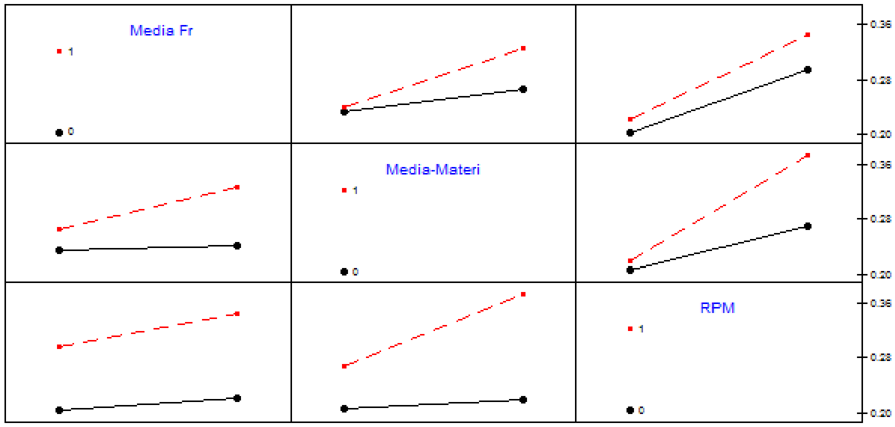

Figure 8. Interaction plot Crystallites vs. Media fraction, Media-Material ratio, and RPM

Additionally, particle size analysis was used to study particle size distribution and agglomeration. Details are presented in Task 3 of this report. Particle size analysis showed the formation of primary and secondary particles (agglomerates).

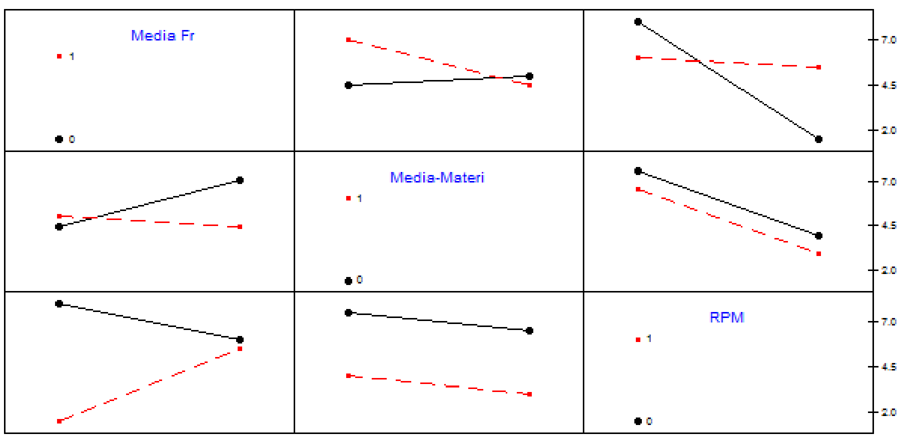

Figure 9. Interaction plot TEM size/shape/dispersity by volume vs. Media fraction, Media-Material ratio, and RPM

Based on the analysis of interactions between synthesis parameters and results from characterization of prepared nanoparticles and combining optimal parameters with optimal time of milling (see more details on milling time in Task 3), the final process parameters will be selected in the next project quarter.

Deliverables

Accomplished Deliverables:

1. Production mill for scale-up installed and in use;
2. Milling media selected and purchased;
3. Synthesis of developed nanolubricant formulations using production mill scale;
4. Design of Experiments developed and used for optimization of scale up process;
5. Optimization of synthesized nanolubricant formulation for scale up;
6. De-agglomeration studies of synthesized nanolubricant formulation.

Task 3: Synthesis, de-agglomeration, and optimization of NanoGlide®

(*Timeline for Task 3: January – August 2010*)

Using parameters from design of experiments and applying them for lab-scale and larger-scale processing equipment at NanoMech to perform the synthesis of nanoparticles, the samples were analyzed toward preparation of uniform, non-agglomerated particles with narrow size distribution and optimal process time.

Results and discussions

For process optimization, the solid lubricant powder was chemo-mechanically milled for various time durations. The oil medium in the selected combination was chosen to allow (a) homogeneous dispersion of particles inside the milling space, thus avoiding particle clogging (b) utilizing mechanical energy to forge interaction between solid and organic agents to provide capping and integration of organic molecules in nanoparticles and (c) capping with organic molecules, reduced agglomeration, and preparing a uniform dispersion with the base oil.

In this project period, two NanoGlide formulations with the same composition prepared in lab-scale and larger-scale mills and dispersed in commercially available formulated gear oil and compared along with the oil by itself. The purpose of this comparison was to investigate whether the nanoparticles prepared in larger-scale can be prepared with less processing time (one sixth, one fourth, one third, or half of lab mill processing time) using optimized parameters of milling. With the comparison of these two samples and the formulated oil by itself, it will be possible see how well our product can work with oils to better the overall task of enhancing lubrication. The morphological comparison of these oils is presented in this task, and tribological comparison is done in the next task through two different types of tribology testing using Pin-on-Disk (POD) and Block-on-Ring (BOR) tests. With these comparisons it can be determined whether the same morphological and tribological properties for NanoGlide prepared in lab-scale mill can be achieved with the larger-scale mill.

Figure 10 shows the sample prepared using the larger-scale mill with 1/6 the processing time of the lab-scale mill. It is clear that significant fracturing of the bulk occurred, but it was not enough to form uniform ellipsoidal nanoparticles with sizes similar to lab mill prepared samples (Figure 1). Particle size analysis (Table 2) also confirms the presence of large size particle fraction (by volume) and still comparatively high mean size of prepared nanoparticles (by number).

The increase of processing time to 1/3 the length of initial lab-scale milling time (Figure 11 and Table 3) and to 1/2 length of initial lab scale milling time (Figure 12 and Table 4) showed a consistent decrease in nanoparticle sizes and formation of ellipsoidal particles.

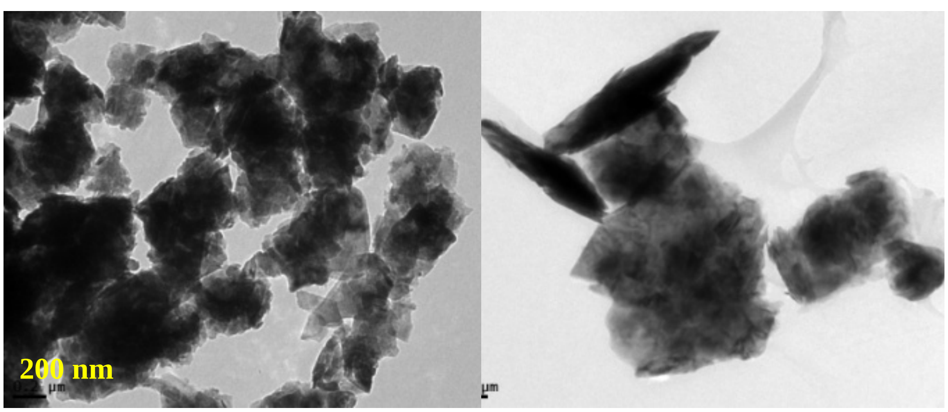

Figure 10. TEM of sample prepared by larger-scale mill (1/6 of initial processing time)

Table 2. PSA of sample prepared by larger-scale mill (1/6 of initial processing time)

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			0.48080 um	0.38384 um	0.2778 um
NG1D2ZX	10	50	90			
	0.2096 um	0.3838 um	0.8754 um			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1.48148 um	1.25747 um	1.2322 um
NG1D2ZX	10	50	90			
	0.5806 um	1.2575 um	2.6898 um			

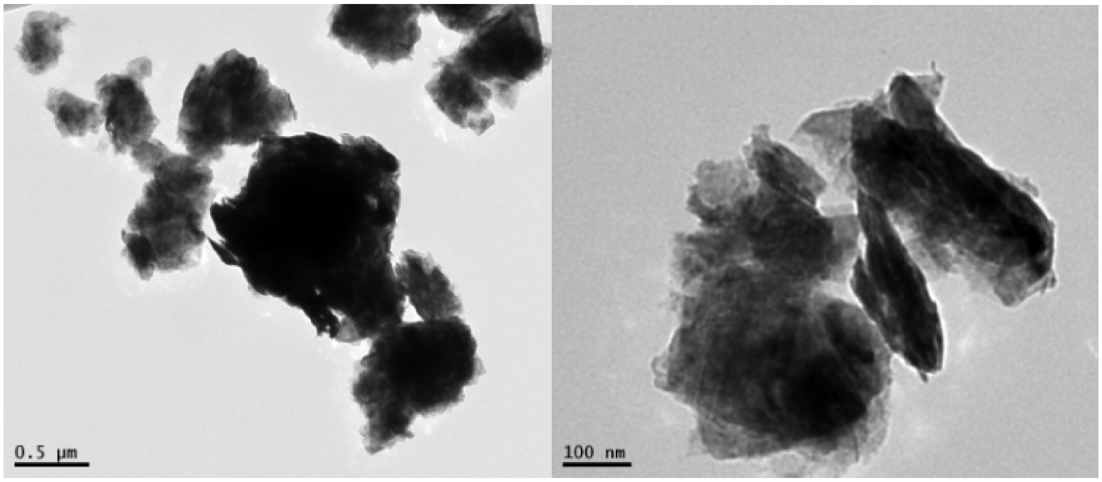

Figure 11. TEM of sample prepared by larger-scale mill (1/3 of initial processing time)

Table 3. PSA of sample prepared by larger-scale mill (1/3 of initial processing time)

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1.31654 um	1.05313 um	1.0734 um
NG1D2ZX	10	50	90			
	0.4457 um	1.0531 um	2.5216 um			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			0.39299 um	0.31964 um	0.2765 um
NG1D2ZX	10	50	90			
	0.1863 um	0.3196 um	0.6955 um			

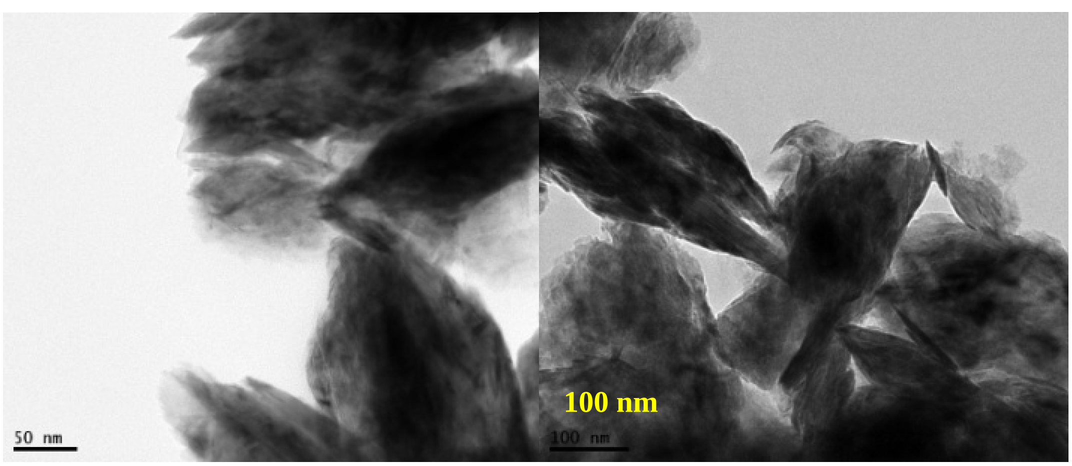

Figure 12. TEM of sample prepared by large scale mill (1/2 of initial processing time)

Table 4. PSA of sample prepared by large scale mill (1/2 of initial processing time)

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1.21562 um	0.89820 um	0.9372 um
NG1D2ZX	10	50	90			
	0.3498 um	0.8982 um	2.4557 um			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			0.32721 um	0.27283 um	0.2425 um
NG1D2ZX	10	50	90			
	0.1669 um	0.2728 um	0.5527 um			

The prepared sample (Figure 12) showed similar structural and morphological characteristics of the nanoparticles as compared to samples prepared using the lab mill. However, runs of 2/3 the length of the initial processing time will be performed to determine whether ½ the length of the initial processing time is sufficient or if longer milling time is necessary to achieve less aggregated samples (Table 4).

Deliverables
Accomplished deliverables:

1. Design of experiments for synthesis and optimization for scale up;
2. Development of NanoGlide® production procedure (also see 1st quarter report);
3. Synthesis of nanolubricants for naval applications;
4. Optimization of scaled-up milling.

Deliverables for 4th quarter of the project:
1. Development of product control procedures;

Task 4: Structural, chemical, and physical analysis of nanostructures and inorganic-organic interfaces

Complementary analytical techniques are applied with particular objectives to study properties of synthesized nanoparticles and scale-up optimization (size and shapes, surface area, nanostructure, and chemical analysis) and tribological performance (tribofilm formation, debris formation, nanoparticles morphology). The structural analysis (size and shapes of nanoparticles) was discussed in the previous task in combination with scale-up discussions. This task covers chemical and physical analysis of nanostructures and the inorganic-organic interface in gear oils and greases, and analysis of formed tribofilms after the tribotesting.

4.1. NanoGlide additives for oil

The initial two formulations of NanoGlide were modified and improved for specific application as additives for gear oils and greases. The components of the nanoparticle additives in gear oil are encoded as follows (numbers in the sample identifications are for unique identification only and do not denote how much of any component was added to the formulation):

Table 5. Modified NanoGlide formulations prepared for gear oil

GY1:	Friction modifier Y (FM)
GT2:	High temperature extreme pressure additive T (HT-EP)
GO3:	Blank Gear Oil (GO)
GXYZ4:	Friction modifier Y, Phospholipid X, EP additive Z (EP)
GTWX5:	HT-EP T, Vegetable oil W (VO), Phospholipid X (PL)
GTYZ6:	HT-EP T, FM Y, EP Z
GZU17:	EP Z, Dispersant U1
GU2Z8:	EP Z, Dispersant U2
GZX9:	Initial formulation 1 of NanoGlide®
GZ10:	EP Z
GV11:	Initial formulation 2 of NanoGlide®

The prepared modified formulations for greases were analyzed using Particle Size Analysis (Table 6) and their tribological performance was studied using Pin-on-Disk and Block-on-Ring tribometers (see Task 5). The Particle size analysis was used to select samples with the smallest sizes of primary nanoparticles and smallest sizes of secondary particles (agglomerates).

Table 6. PSA of Modified NanoGlide Formulations

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
GY1	Diameter on Cumulative %			1490 nm	729 nm	477 nm
	10	50	90			
	313 nm	729 nm	3310 nm			

Particle Size Analysis	**Distribution Base: Number**			**Mean Size**	**Median Size**	**Mode Size**
GY1	Diameter on Cumulative %			327 nm	290 nm	277 nm
	10	50	90			
	190 nm	290 nm	500 nm			

Particle Size Analysis	**Distribution Base: Volume**			**Mean Size**	**Median Size**	**Mode Size**
	Diameter on Cumulative %			916 nm	585 nm	318 nm
GYZ12	10	50	90			
	230 nm	585 nm	2020 nm			

Particle Size Analysis	**Distribution Base: Number**			**Mean Size**	**Median Size**	**Mode Size**
	Diameter on Cumulative %			238 nm	207 nm	184 nm
GYZ12	10	50	90			
	140 nm	207 nm	366 nm			

Particle Size Analysis	**Distribution Base: Volume**			**Mean Size**	**Median Size**	**Mode Size**
	Diameter on Cumulative %			1500 nm	1100 nm	1230 nm
GXYZ13	10	50	90			
	329 nm	1096 nm	3212 nm			

Particle Size Analysis	**Distribution Base: Number**			**Mean Size**	**Median Size**	**Mode Size**
	Diameter on Cumulative %			263 nm	216 nm	184 nm
GXYZ13	10	50	90			
	140 nm	216 nm	432 nm			

Particle Size Analysis	**Distribution Base: Volume**			**Mean Size**	**Median Size**	**Mode Size**
	Diameter on Cumulative %			2390 nm	1550 nm	1410 nm
GXYZ4	10	50	90			
	470 nm	1550 nm	5420 nm			

Particle Size Analysis	**Distribution Base: Number**			**Mean Size**	**Median Size**	**Mode Size**
	Diameter on Cumulative %			303 nm	237 nm	185 nm
GXYZ4	10	50	90			
	153 nm	237 nm	524 nm			

Particle Size Analysis	**Distribution Base: Volume**			**Mean Size**	**Median Size**	**Mode Size**
	Diameter on Cumulative %			606 nm	429 nm	278 nm
GT2	10	50	90			
	190 nm	429 nm	1240 nm			

Particle Size Analysis	**Distribution Base: Number**			**Mean Size**	**Median Size**	**Mode Size**
	Diameter on Cumulative %			203 nm	179 nm	161 nm
GT2	10	50	90			
	125 nm	179 nm	306 nm			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1160 nm	667 nm	363 nm
GTX4	10	50	90			
	247 nm	667 nm	2790 nm			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			243 nm	214 nm	185 nm
GTX4	10	50	90			
	144 nm	214 nm	372 nm			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1350 nm	832 nm	821 nm
GTWX5	10	50	90			
	272 nm	832 nm	3060 nm			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			266 nm	223 nm	185 nm
GTWX5	10	50	90			
	144 nm	223 NM	429 nm			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			703 nm	443 nm	276 nm
GTYZ6	10	50	90			
	179 nm	443 nm	1550 nm			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			193 nm	170 nm	159 nm
GTYZ6	10	50	90			
	121 nm	170 nm	287 nm			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1340 nm	1020 nm	1230 nm
GU1W14	10	50	90			
	295 nm	1020 nm	2810 nm			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			248 nm	202 nm	162 nm
GU1W14	10	50	90			
	135 nm	202 nm	405 nm			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			2350 nm	1790 nm	1620 nm
GU1Z7	10	50	90			
	628 nm	1790 nm	4840 nm			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			332 nm	237 nm	162 nm
GU1Z7	10	50	90			
	149 nm	238 nm	641 nm			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			2200 nm	1830 nm	1850 nm
GU2W15	10	50	90			
	782 nm	1830 nm	4150 nm			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			502 nm	365 nm	197 nm
GU2W15	10	50	90			
	197 nm	365 nm	992 nm			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1790 nm	1410 nm	1610 nm
GU2Z8	10	50	90			
	442 nm	1410 nm	3700 nm			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			322 nm	257 nm	241 nm
GU2Z8	10	50	90			
	160 nm	257 nm	555 nm			

In general, almost all modified formulations had nanoparticles with similar morphological characteristics to nanoparticles from the initial formulations. However, several of the samples with the modified formulations showed significant improvement in achieving smaller sizes of nanoparticles (Table 6, samples GYZ12, GT2, GTYZ6) and less aggregated secondary particles (samples GYZ12, GT2, GTYZ6).

4.2. NanoGlide additives for grease

NanoGlide nanoparticles were used as an additive for greases and their structural and tribological properties were studied (Four Ball Test).

Two different formulations of NanoGlide (NanoGlide 1 ZX and NanoGlide 2 WX) were used as additives in extreme pressure lithium–base grease (EP Li-base grease) for comparison with performance of neat base grease and base grease formulated with commercially available MoS_2 (micron size nanoparticles) and commercially available WS_2 nanoparticles. Concentration of all additives was kept constant in terms of weight percentage of the solid phase.

4.2.1 Morphological and compositional analysis of grease tribofilms through Scanning Electron Microscopy (SEM)/ Energy-dispersive X-ray spectroscopy (EDX)

The 4 Ball wear test is the predominant wear tester used to study the chemical interactions occurring at wearing contacts for greases. The wear tracks generated on one of the stationary balls from the 4 Ball wear test were observed under the Nova SEM.

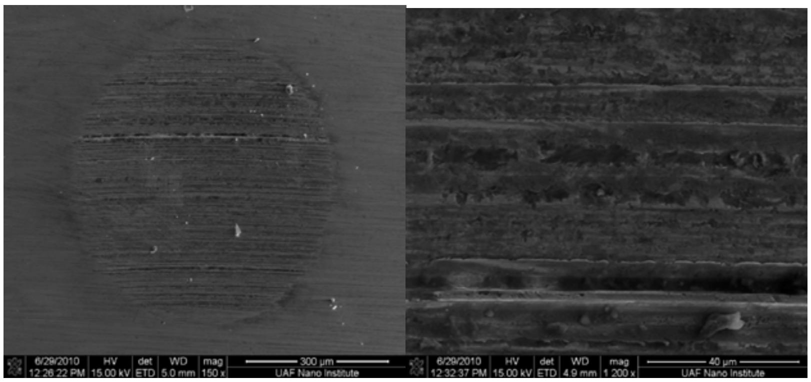

Figure 13. SEM of wear for base grease 4 Ball test

As can be observed below, the wear track showed presence of grooves running parallel to the direction of sliding, plastic flow, and fine wear debris, all indicative of the occurrence of abrasive wear. There is some pull-out seen on the track suggesting that some adhesive wear could have taken place at regions where the tribofilm was formed insufficiently or was weakly adherent to the surface. The EDX analysis shows the elemental composition of EP Li-base grease (Figure 14) that was used as a base grease for NanoGlide additives.

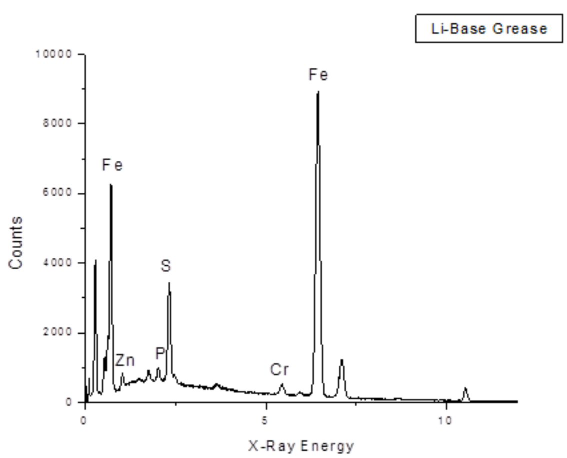

Figure 14. EDX spectrum of wear for EP Li-base grease using 4 Ball test

From the elemental maps, the distribution of elements on the tribofilm can be seen. The film formed through the base grease shows the presence of phosphorus and sulfur. The presences of these elements were also confirmed through the EDX spectrum. These elements are main components of extreme pressure additives in greases.

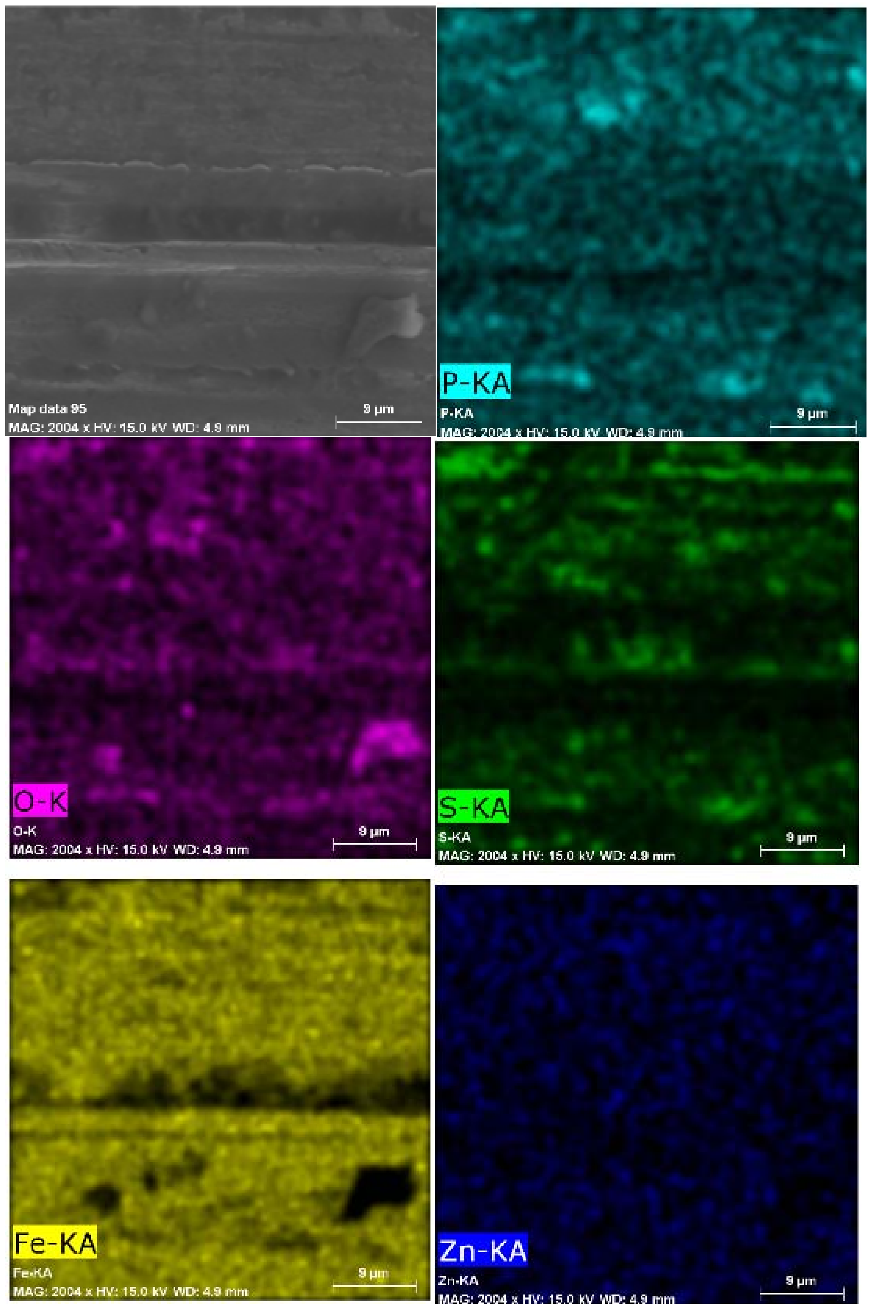

Figure 15. SEM and EDX elemental mapping (phosphorous, oxygen, sulfur, iron and zinc) of wear region for base grease 4 Ball test

Base grease was formulated with commercially available molybdenum sulfide powder from bulk using the same weight percentage of solid phase as was used for greases formulated with nanoparticles. From the images above, it can be concluded that wear occurred mostly through abrasion. At some regions pull-out of the tribofilm can be seen suggesting that either the tribofilm was incompletely formed or was weakly bonded to the substrate.

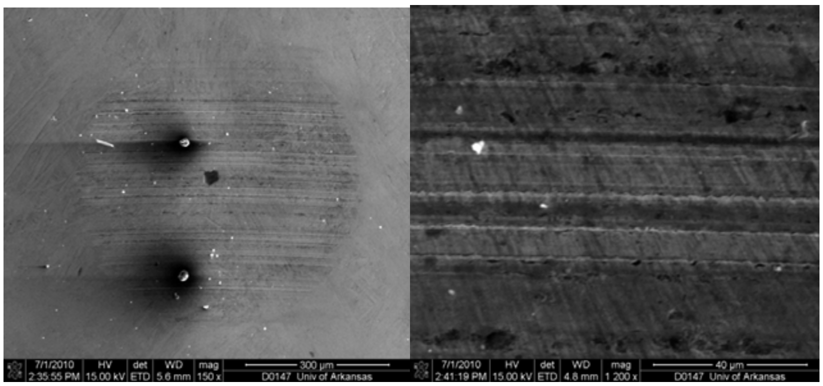

Figure 16. SEM of wear for base grease and MoS_2 microparticles 4 Ball test

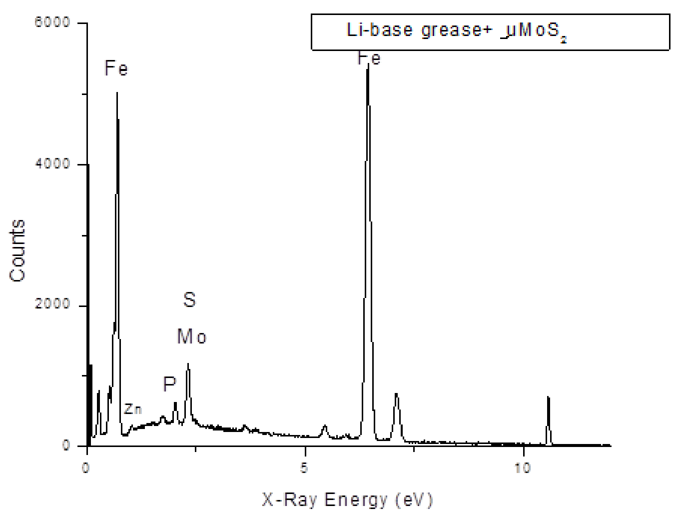

Figure 17. EDX spectrum of wear for EP Li-base grease with MoS_2 microparticles using 4 Ball test

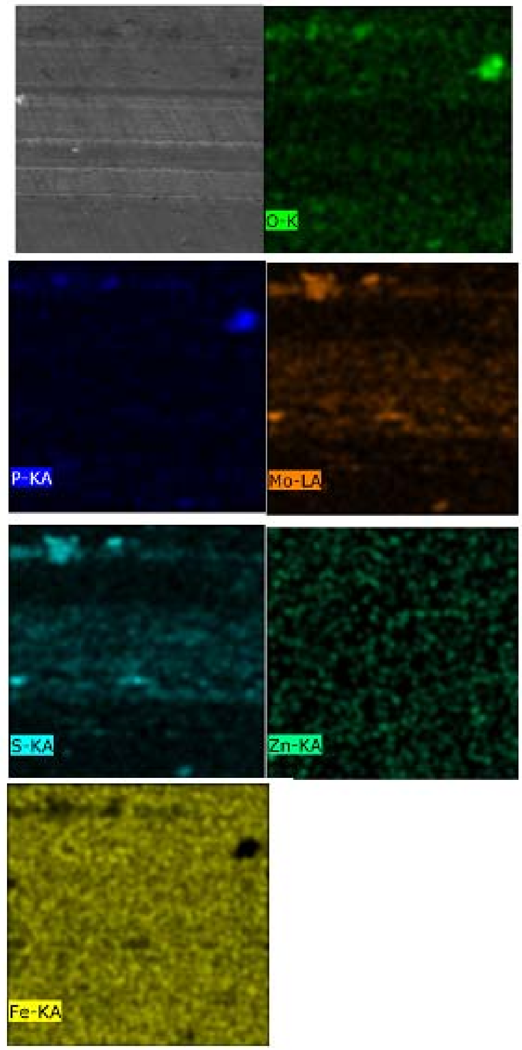

Figure 18. SEM and EDX elemental mapping (oxygen, phosphorous, molybdenum, sulfur, zinc, and iron) of wear region for base grease and MoS_2 microparticles 4 Ball test

From the above maps, there can be seen localized distribution of Mo and S suggesting the formation of MoS_2 tribofilms. The occurrence of P and O at similar locations on the tribofilm may suggest the formation of phosphates.

The tribofilms formed from NanoGlide 1 ZX in grease showed less abrasive wear, some pull-out, and plastic deformation. There was incorporation of wear debris in the grooves that may provide additional benefit of supporting some part of the load and/or act to help in sliding by acting as miniature ball-bearings.

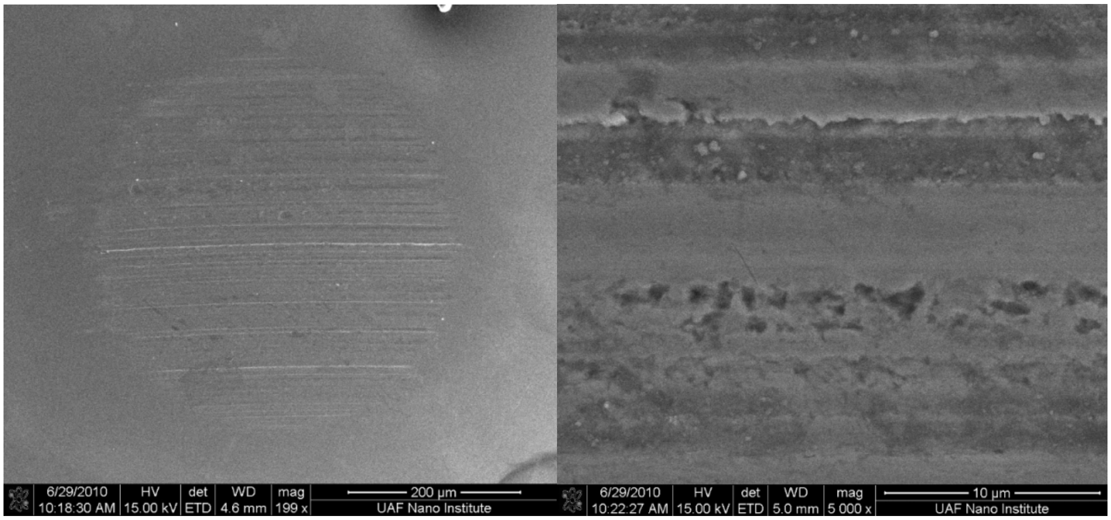

Figure 19. SEM of wear for base grease and NanoGlide 1 ZX using 4 Ball test

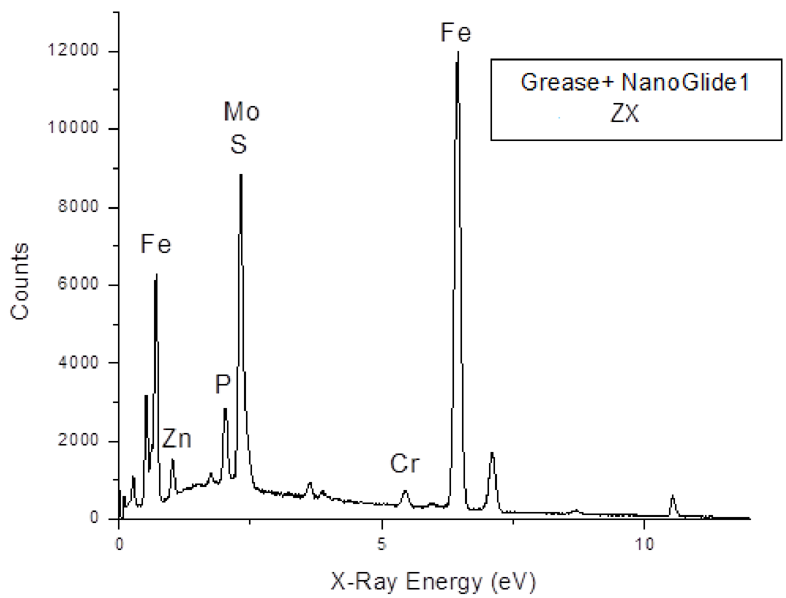

Figure 20. EDX spectrum of wear for EP Li-base grease and NanoGlide 1 ZX using 4 Ball test

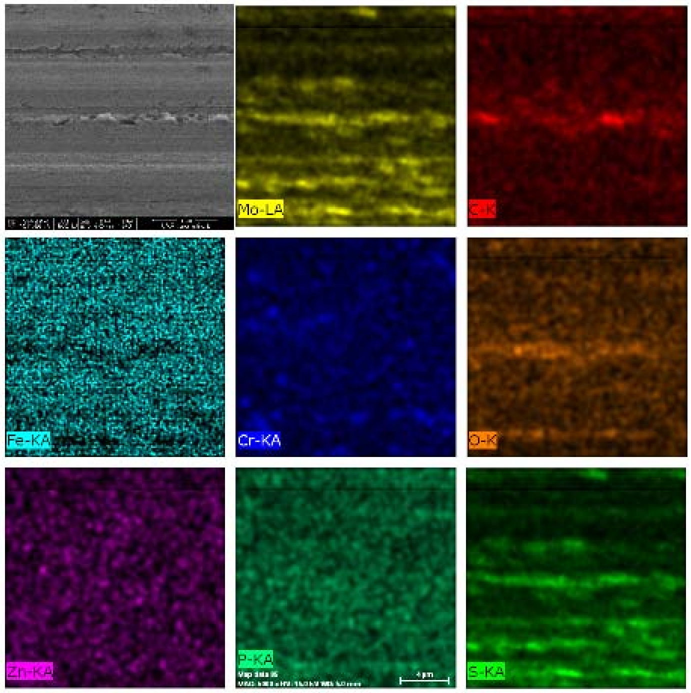

Figure 21. SEM and EDX elemental mapping (molybdenum, carbon, iron, chromium, oxygen, zinc, phosphorous, and sulfur) of wear region for base grease and NanoGlide 1 ZX using 4 Ball test

The occurrence of Mo and S at the wear tracks was indicative of the formation of an MoS_2 tribofilm. Not much information is available to draw conclusions on the formation of phosphates or other compounds.

As is observed from the elemental maps, there could be formation of a patchy tribofilm of MoS_2 on the substrate since lesser signals are obtained from Fe in the same regions. There could also be some formation of phosphates since P and O occur at similar locations on the surface.

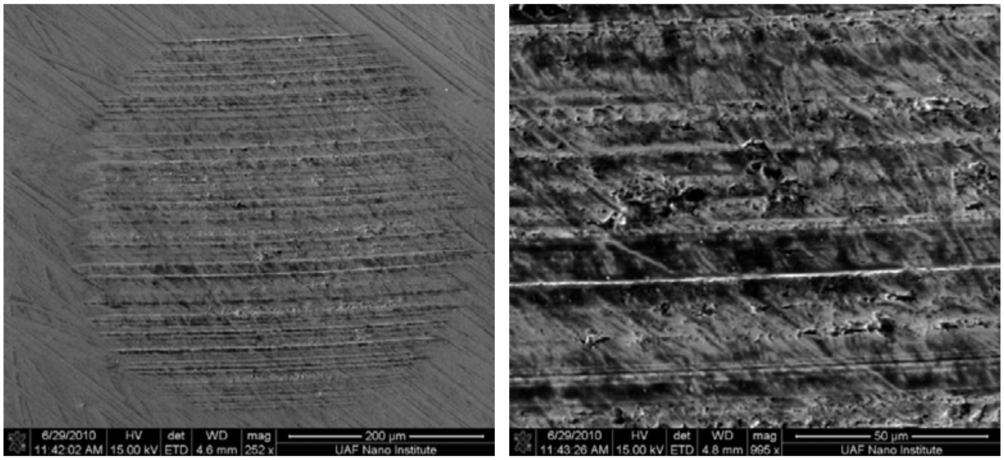

Figure 22. SEM of wear for base grease and NanoGlide 1 ZX using 4 Ball test

Shown below are the SEM images of grease containing NanoGlide 2 WX. Mild abrasive wear and a few regions of pull-out can be observed. In the cavities formed, there is deposition of either debris or some particles that could help support a part of the load.

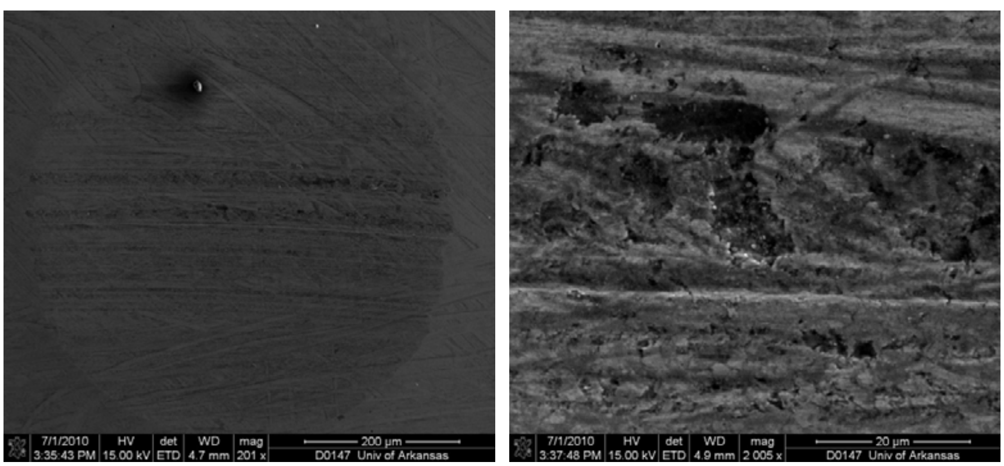

Figure 23. SEM of wear for base grease and NanoGlide 2 WX using 4 Ball test

EDS was performed on the area of the tribofilm shown in the inset picture. The Zn from the grease participates in the formation of the tribofilm. The elemental maps below show the distribution of the elements on the tribofilm formed from NanoGlide 2 WX.

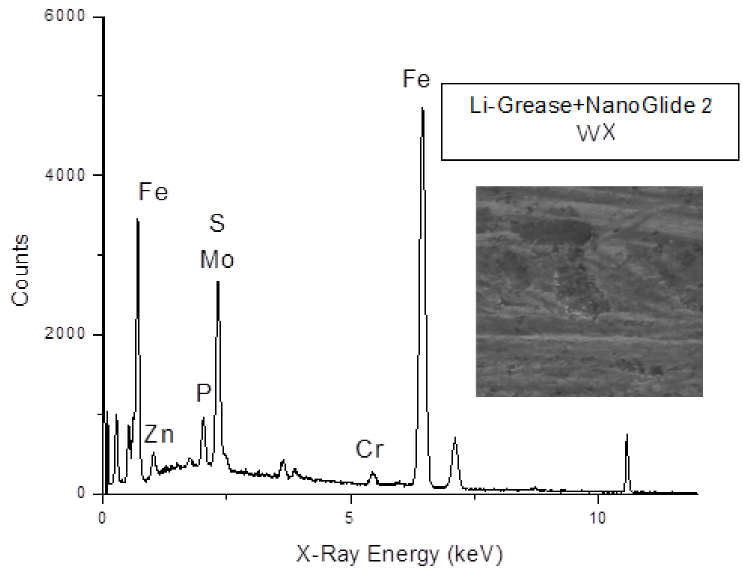

Figure 24. EDX spectrum of wear for EP Li-base grease and NanoGlide 2 WX using 4 Ball test

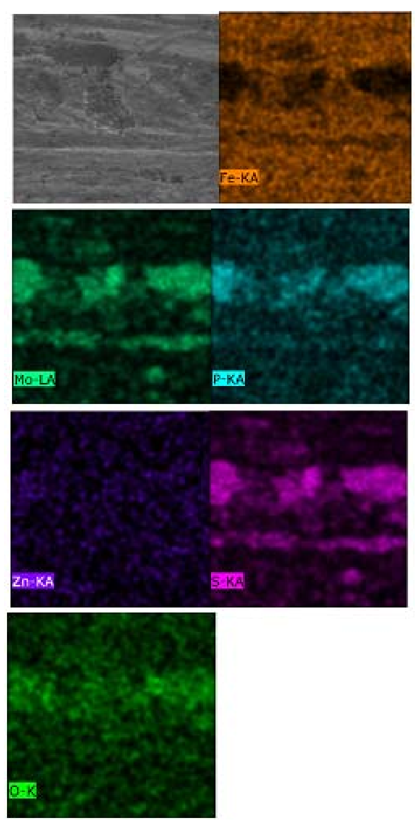

Figure 25. SEM and EDX elemental mapping (iron, molybdenum, phosphorous, zinc, sulfur, and oxygen) of wear region for base grease and NanoGlide 2 WX using 4 Ball test

As seen from the elemental maps, in the regions of pull-out cavities, there could be deposition of MoS_2 film and/or phosphates. The lesser signal received from Fe may suggest that there could be less formation of iron compounds in the cavities.

Base grease was formulated with commercially available tungsten sulfide powder from nanoparticles using the same weight percentage of solid phase as with the greases formulated with NanoGlide nanoparticles. The SEM wear track indicates that the tribofilm is very patchy with mild abrasive wear and presence of wear debris/ particles in the grooves/ cavities.

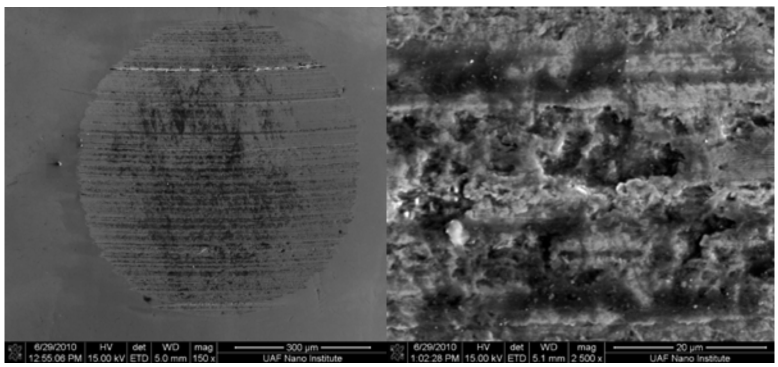

Figure 26. SEM of wear for base grease and WS_2 nanoparticles using 4 Ball test

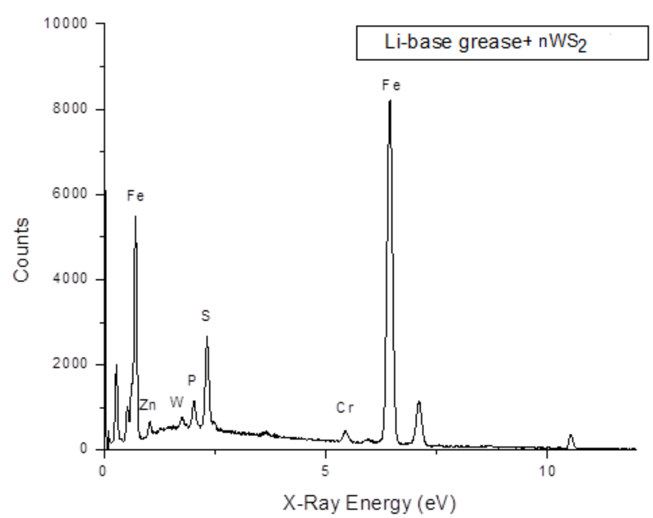

Figure 27. EDX spectrum of wear for EP Li-base grease and WS_2 nanoparticles using 4 Ball test

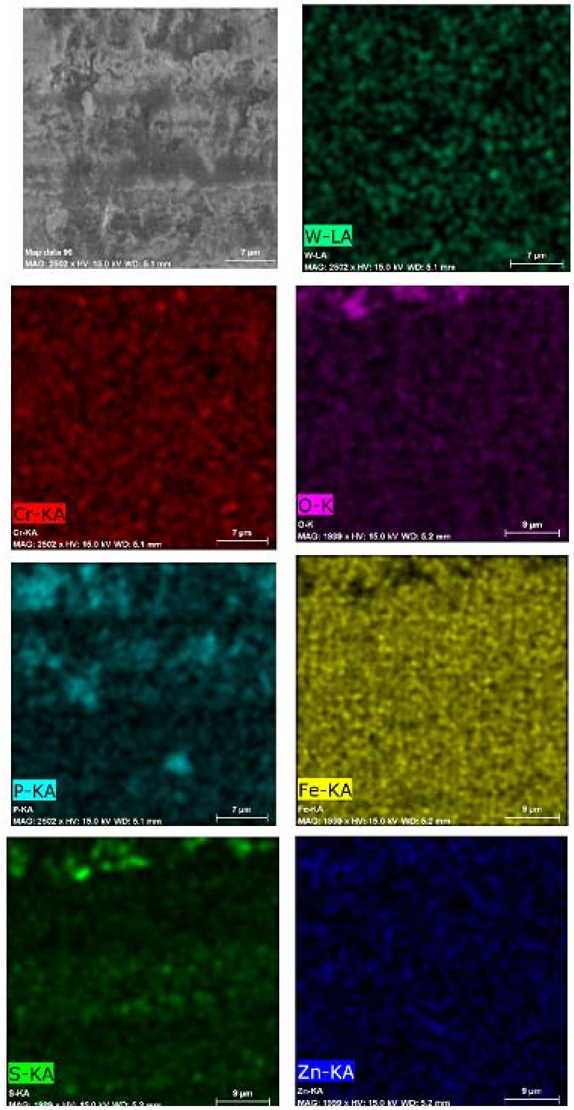

Figure 28. SEM and EDX elemental mapping (tungsten, chromium, oxygen, phosphorous, iron, sulfur, and zinc) of wear region for base grease and WS_2 nanoparticles using 4 Ball test

The elemental maps indicate that there is localized occurrence of phosphorus and sulfur that could be present as phosphates, sulfides, and sulfates. The presence of some amounts of zinc could be from the base grease which contains 5-10% zinc compounds.

Conclusions

Tribofilms from NanoGlide 1 ZX and NanoGlide 2 WX show mild abrasive wear and that from NanoGlide 2 and WS_2 appear patchy with cavities.

Only qualitative information was obtained from the EDS data and to understand the nature of bonding of different elements, further characterization like XPS/Auger, was performed and analysis of data will be presented in the next report.

Task 5**: Tribological testing of NanoGlide**

Tribological testing was conducted using bench-top tribological test setups (Block-on-Ring, Pin-on-Disc, 4 Ball, and Extreme Pressure 4 Ball tests) focusing on boundary lubrication conditions.

5.1. Tribological performance of nanolubricant in gear oils

The lubrication performance of gear oils and greases with nanoparticle (NanoGlide®) additives was studied through tribological testing. The test results were used to generate friction and wear maps demonstrating the useful tribological performance and to compare performance of nanoparticles in gear oils and greases. The tribological testing and tribofilm analysis were used to understand the behavior of the additives in the oil blend and to develop the final nanoparticles-based formulation for use in the target applications.

In this reporting period, modified NanoGlide formulations were added to gear oils to evaluate and compare their performance. The gear oils were specifically selected to see the direct effect of MoS_2 nanoparticle addition on the formulated oil. Tribological performance of nanoparticles in both gear oils and grease will be reported in this report period.

Block on ring tribotesting

A CETR tribometer model UMT-3 with a Block-on-Ring driver configured for a self-leveling block (SLB) was used for tribotesting. The self-leveling block consisted of a holder for the block to maintain its position, resting on the ring, while a pin modified the load from above.

Each test consisted of a different lubricant and three, consecutively performed steps. The first step, after centering the carriage to press the block, consisted of applying thirty-three kilograms worth of force on the block. Afterwards, the ring was spun at one thousand rpm for a full minute to warm-up and break-in the operating components (ring, block, driver, etc.). Finally, data for temperature and coefficient of friction (COF) were collected for comparison during the final step: a run at five hundred rpm lasting thirty minutes.

Each graph (Figure 29 and 30) consists of plots labeled according to their formulation (GF refers to formulated gear oil G, GNF refers to non-formulated gear oil (neat), and GNG refers to gear oil formulated with NanoGlide® ZX; index 1 refers to the first run and index 2 refers to the second run).

The graphs each consist of raw data from the tribometer that have been reduced through averaging by a factor of one-hundred twenty for the sake of visual representation.

Table 7 summarizes the tribological performance of gear oils - non-formulated (NF) and formulated (F) and formulated gear oil with NanoGlide ZX additive (NG). It is clear that gear oil with NanoGlide is the leader in smallest coefficient of friction, lowest oil temperature, and smallest wear scar area.

Table 7. Tribological performance of gear oils and NanoGlide ZX

Sample	Average COF, µ	Maximum Temperature, °C	Wear, mm^2
NF	0.126	49.5	6.37
F	0.112	51.3	3.10
NG	0.094	43.2	2.63

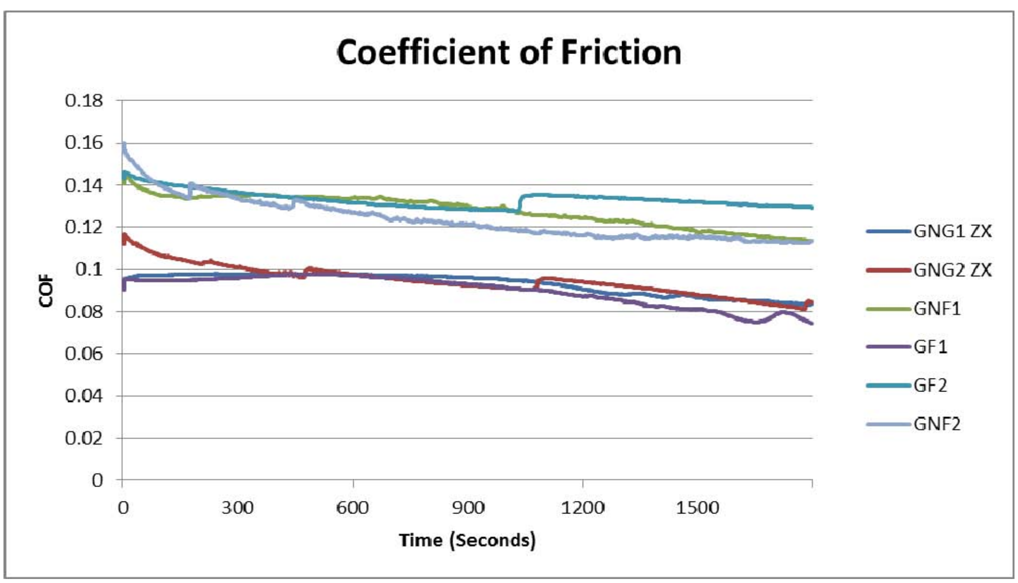

Figure 29. COF comparison for gear oils and NanoGlide ZX using Block-on-Ring test

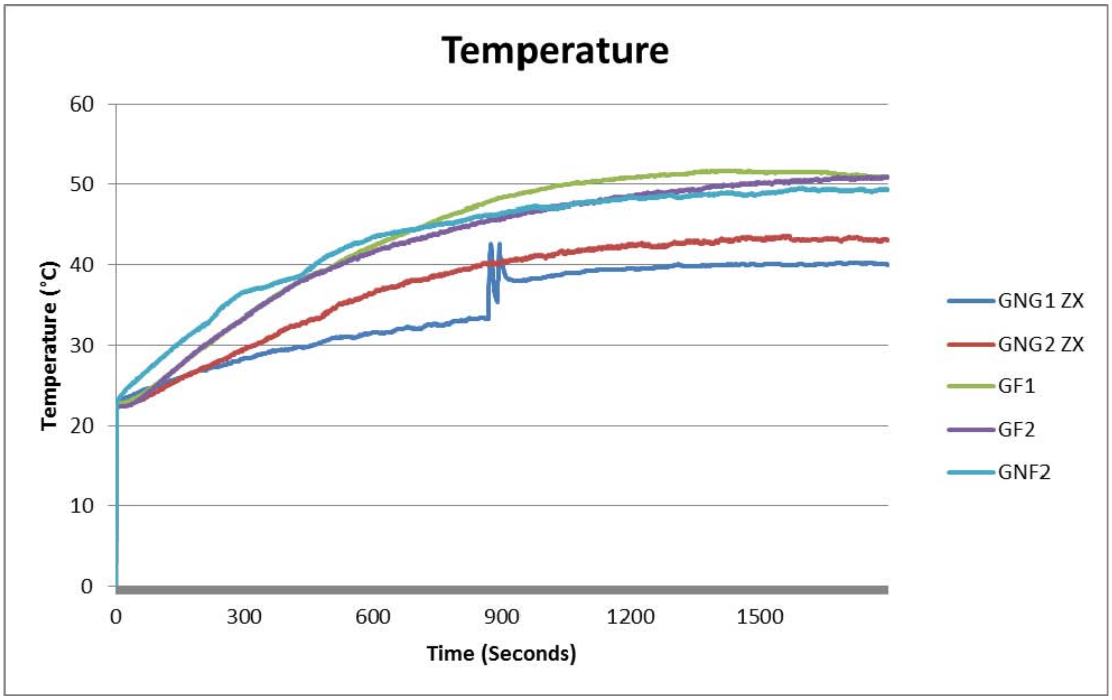

Figure 30. Temperature comparison for gear oils and NanoGlide ZX using Block-on-Ring test

Following tribotesting, the blocks were SEM imaged and the surface wear scar was measured using an optical microscope. SEM pictures and microscope pictures were taken of the wear scars to assess how well the blocks were lubricated. The images from the optical microscope are not precise, and further study should be done using a profilometer.

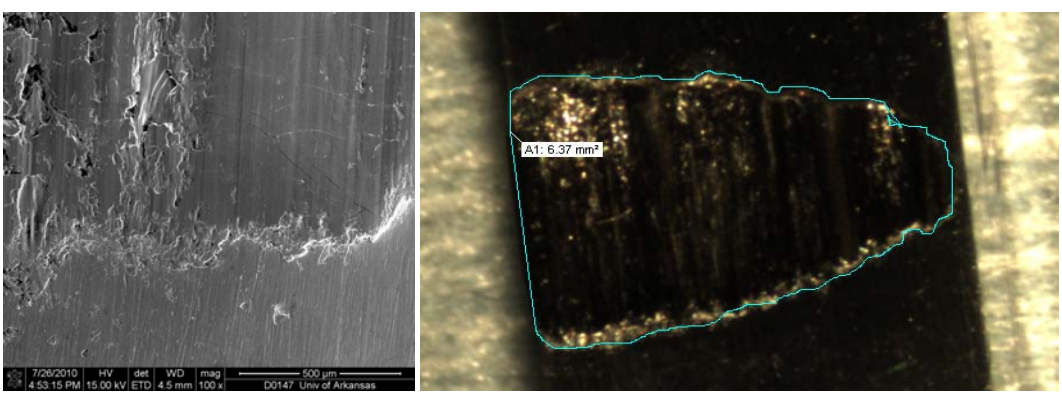

Figure 31. SEM image (left) and optical microscope image with wear surface (right) on block for non-formulated gear oil (NF)

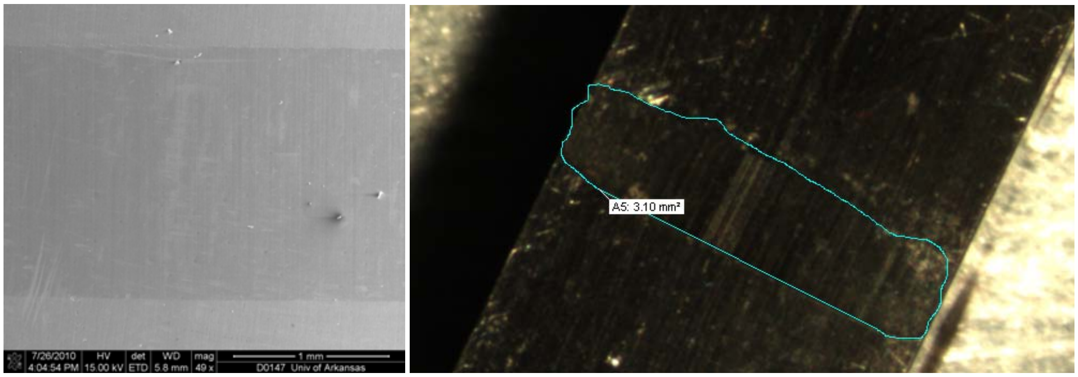

Figure 32. SEM image (left) and optical microscope image with wear surface (right) on block for formulated gear oil

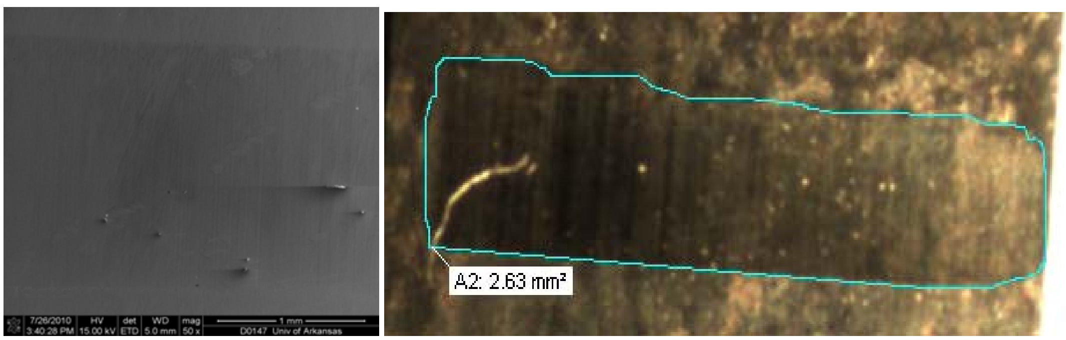

Figure 33. SEM image (left) and optical microscope image with wear surface (right) on block for formulated gear oil with NanoGlide ZX (NG)

In terms of reproducibility, the results show very little difference between testing runs for the same samples. This finding, along with the values of standard deviation and average percent difference, indicates good consistency in the test results.

In terms of tribological performance, NanoGlide® ZX formulated oils performed best in terms of their coefficient of friction, in oil temperature over time, and measured wear scar area. The wear scar data for all tests was collected by optical microscope measurements, and generally follows and supports the trend in the rest of the data for wear.

The modified formulations of NanoGlide (see section 4.1 and Table 5) were prepared and added to formulated gear oil. Figures 34 and 35 give a good representation of these formulations for lubrication performance and temperature of oils during Block-on-Ring testing. There is correspondence between a higher temperature and a higher coefficient of friction. This is so because as more wear occurs, the kinetic energy of the interaction is transferred to the surrounding oil.

As a final addendum to the analysis of the Block-on-Ring testing, the surface areas of the wear scars on the blocks were measured from the wear images, which proved to be difficult to read at best. The larger wear scars do seem to correspond with the higher coefficients of friction and temperatures. Therefore, the best formulation is one with the least amount of wear, which would come from the lowest friction and lowest temperature category (e.g., GTYZ6, GU2Z8, and GXYZ4).

Table 8. Tribological performance of gear oil with modified formulations of NanoGlide using Block-on-Ring Test

Samples	COF	Temperature, °C	Surface Wear, mm^2
GY1	0.059	34.3	2.20
GT2	0.062	50.4	2.21
GO3	0.081	51.5	2.84
GXYZ4	0.059	48.3	2.04
GTWX5	0.062	43.1	2.42
GTYZ6	0.071	49.0	2.03
GZU17	0.070	44.4	2.73
GU2Z8	0.057	41.5	2.53
GZX9	0.080	45.3	3.02
GZ10	0.073	52.1	2.79
GV11	0.079	51.2	2.25

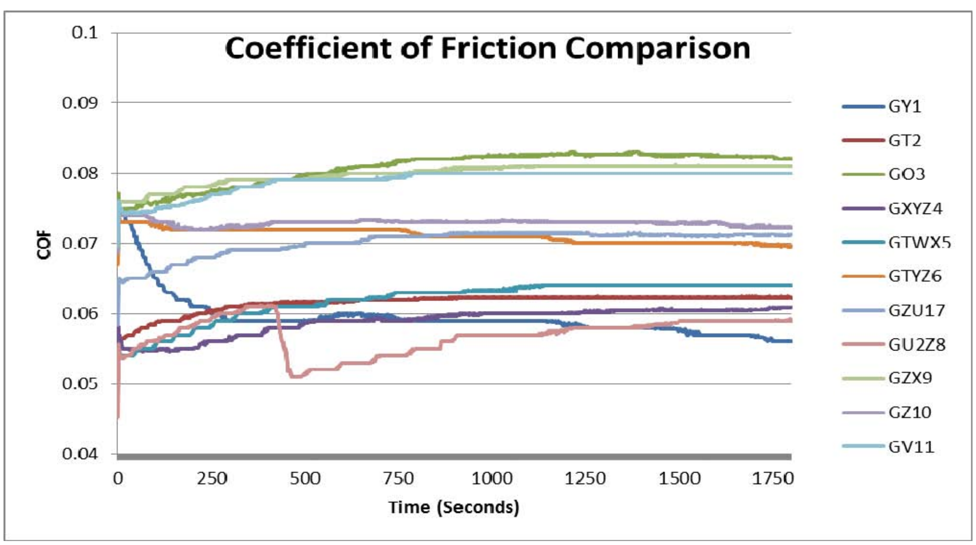

Figure 34. COF comparison for gear oil and modified NanoGlide formulations using Block-on-Ring test

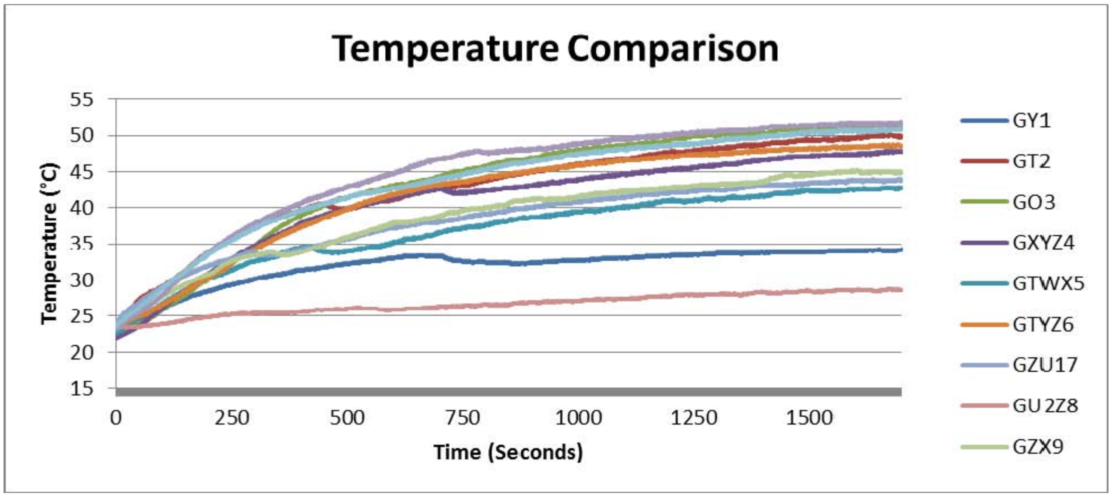

Figure 35. Temperature comparison for gear oil and modified NanoGlide formulations using Block-on-Ring test

Drawing from the results listed above, the most effective formulations with the formulated oil were GY1 and GU2Z8. These two were ranked best because both have the lowest temperature and lowest coefficient of friction readings. In contrast, GO3, GZ10, and GV11 had some of the poorest rankings because they all exhibited high temperatures and high coefficients of friction. Between the two extremes, the only other oils that could be looked into for any more precise results would be GTWX5, GXYZ4, and GT2 since each had either a low final temperature or a low coefficient of friction.

Pin on Disk Testing

Gear oils with modified NanoGlide formulation were tested on the CSM pin/ball-on-disk tribometer. Each test has duration of sixty minutes, surface speeds of 100 rpm, and load of 20 N.

In the analysis of this data, the best formulations give the lowest coefficient of friction (Figure 36 and Table 9). When analyzing the images of the wear scar, a smaller radius indicates better performance of the lubricant (Figures 37-39).

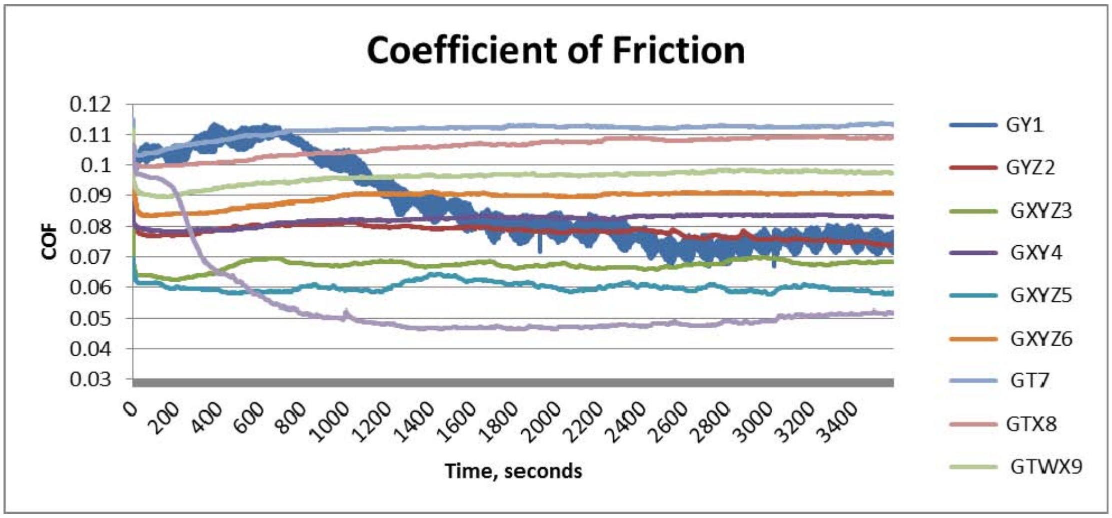

Figure 36. COF comparison for gear oil and modified NanoGlide formulations using Pin-on-Disk test

Table 9. Tribological performance of gear oil with modified formulations of NanoGlide using Pin-on-Disk Test

Samples	COF, µ	Wear Scar, µm
GY1	0.088	152.9
GYZ2	0.078	140.7
GXYZ3	0.067	153.6
GXY4	0.082	134.6
GXYZ5	0.060	153.0
GXYZ6	0.089	122.5
GT7	0.111	125.1
GTX8	0.106	143.5
GTWX9	0.096	106.6
GTYZ10	0.054	139.3

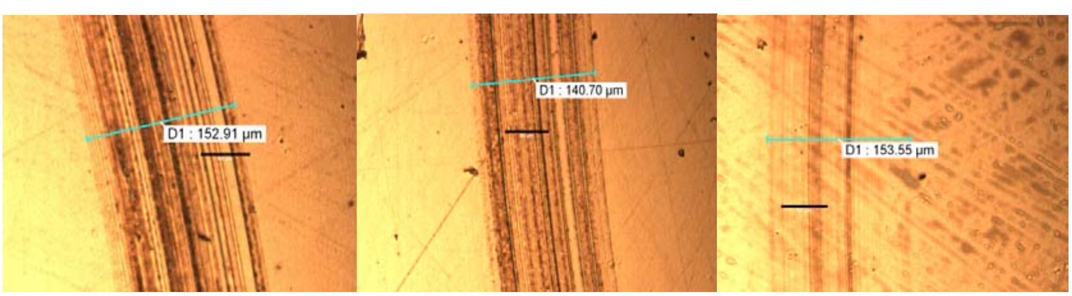

Figure 37. Optical microscope image with wear surface on disc for formulated gear oil with NanoGlide formulations (GY1, GYZ2, and GXYZ3)

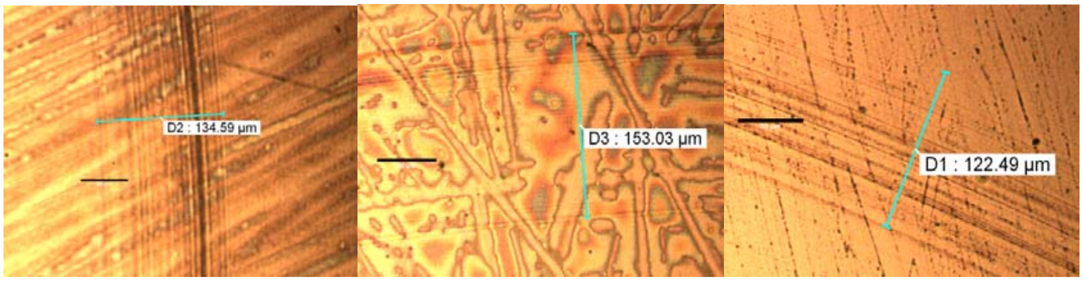

Figure 38. Optical microscope image with wear surface on disc for formulated gear oil with NanoGlide formulations (GXY4, GXYZ5, and GXYZ6)

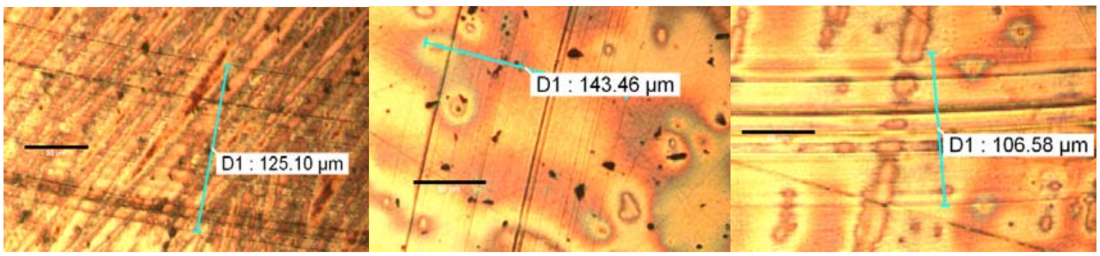

Figure 39. Optical microscope image with wear surface on disc for formulated gear oil with NanoGlide formulations (GT7, GTX8, and GTWX9)

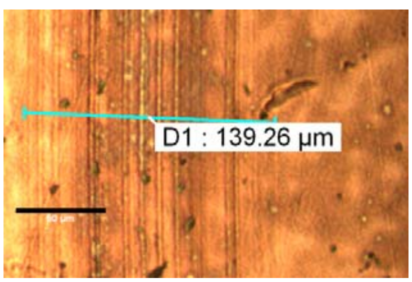

Figure 40. Optical microscope image with wear surface on disc for formulated gear oil with NanoGlide formulation (GTYZ10)

In the presented wear images for NanoGlide GT-based formulations (GT7, GTX8, GTX8, GTWX9, and GTYZ10), the highest coefficient of friction corresponded to the smallest wear scar. Reasons for this might be a deeper wear scar than the picture can capture in two dimensions. Surface profilometry and wear volume measurements may give a better understanding of the lubrication and wear mechanisms for these formulations. The specimen tribofilms were analyzed using XPS, Auger, and TOF-SIMSD and results will be presented in the next report.

Using the coefficient of friction rankings for the Pin-on-Disk tribotesting, the best additives were GT7 and GTYZ10. Performance for both of these additives corresponded well to their particle size analysis (PSA) results and also gave fairly good results in the Block-on-Ring test.

In summary, the tribotesting results of gear oils with NanoGlide formulations should be considered ongoing, as more data is collected for chemical analysis of tribofilms using analytical techniques like XPS, Auger, and TOF-SIMS. More testing of the lubricant additives will be done using Pin-on-Disk, combined with Raman Spectroscopy and FZG testing in the fourth quarter. The results are encouraging, and further information developed in the next reporting period will undoubtedly provide even better understanding of the NanoGlide additive performance in gear oils.

5.2. Tribological performance of nanolubricant in greases

The following table summarizes the list of additives that were added to base grease (NLGI-2 EP Li-base grease with 5-10 weight % of zinc compounds) and tested for tribological performance using the 4 Ball test and EP 4 Ball Test.

Table 10. Grease samples for tribological testing using 4 Ball and EP 4 Ball Tests

Grease
Grease +μ-MoS_2
Grease +n-WS_2
Grease + NanoGlide 1 ZX
Grease + NanoGlide 2 WX

Four Ball Test (ASTM D2266)

The greases were tested for wear efficacy following the ASTM D 2266 standard with conditions of 40 kg load, 1200 rpm and 1 hour test duration.

As is observed from Figure 41, the base grease gave a wear scar diameter of 0.6mm. Adding MoS_2 (micron-sized particles) did little to improve the performance of the base grease. However, significant reduction in the wear scar diameters was observed when NanoGlide 1 ZX and NanoGlide 2 WX were added to the grease. Nanoparticles of WS_2, on the other hand, showed antagonistic behavior, giving a wear scar diameter ~10% greater than that obtained with the base grease.

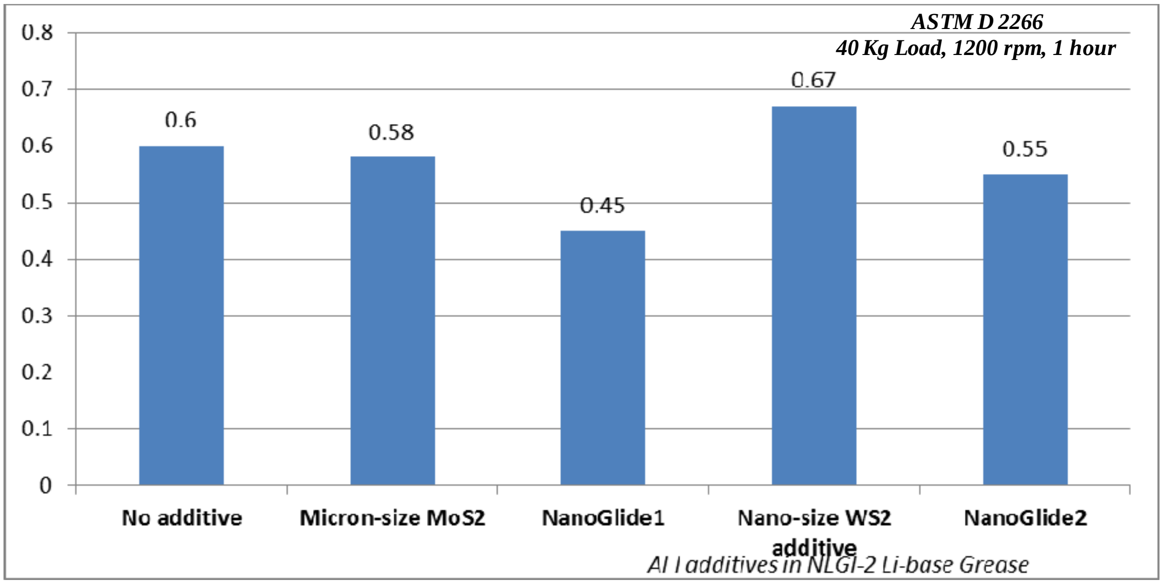

Figure 41. Wear scar diameter comparison for greases using 4 Ball test

<u>EP Four Ball Test (ASTM D2596)</u>

This method is used to determine the load-carrying properties of lubricating greases. Two key results are obtained with this method - Load Wear Index and Weld Load. The rotating speed of the spindle is 1770 +/- 60 rpm. Lubricating greases are brought to 27 +/- 8 °C and then subjected to a series of tests of 10 second durations at increasing loads until welding occurs.

Load wear index (LWI) is the measure of the relative ability of the lubricant to prevent wear under applied loads. As seen in Figure 42, NanoGlide 1 ZX shows the highest LWI indicating that the benefit of NanoGlide is realized.

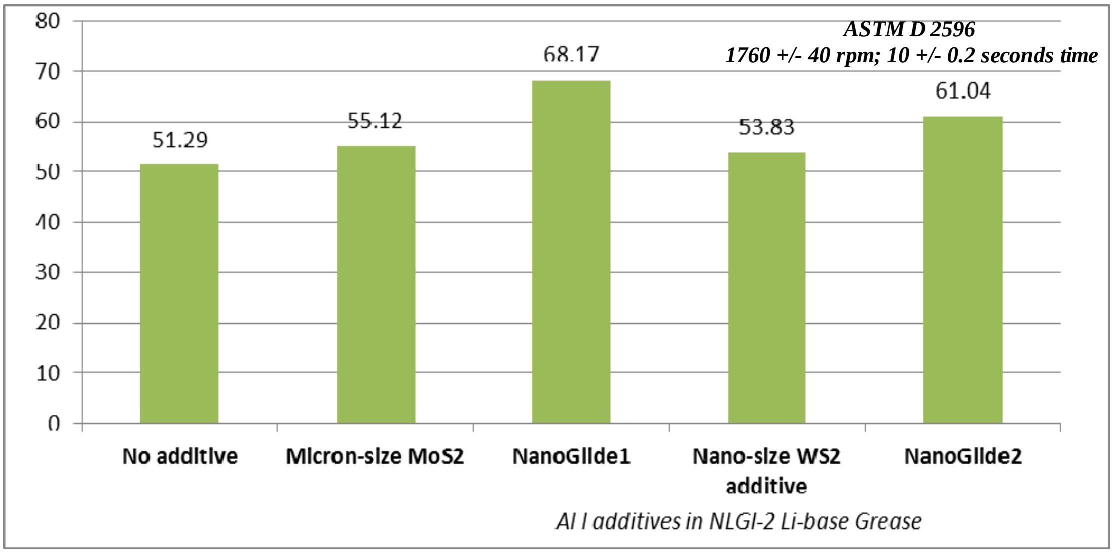

Figure 42. LWI comparison for greases using 4 Ball test

The Weld Point is the lowest applied load in kilograms at which the rotating ball in the Four Ball EP test either seizes and welds to the three stationary balls, or results in extreme scoring of the three balls. It is a measure of the extreme pressure properties of the lubricants.

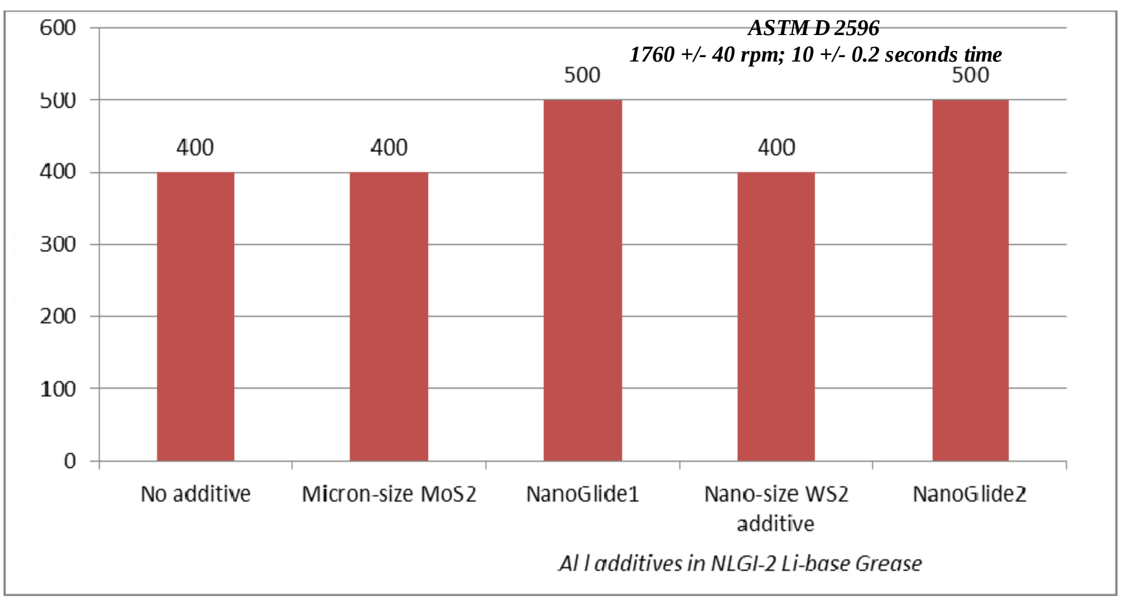

Figure 43. Weld point comparison for greases using 4 Ball test

All of the NanoGlide versions in grease gave better wear and LWI performance than neat grease, grease with WS_2 nanoparticles and grease with MoS_2 micron size particles. Among all of the five greases tested, grease with NanoGlide 1 ZX proved to be the best with the lowest wear scar numbers and highest LWI and weld load.

5.3 Analysis and testing of structure-properties-application relationship *(University of Arkansas subcontract)*

The University of Arkansas is investigating the performance of nanolubricants when added into gear oils, using a Pin-on-Disk test and a test vehicle based on a real gearbox housing (FZG test).

<u>Pin/Ball-on-Disk tribotesting</u>

Gear oils (premium gear oil and non-premium oil with NanoGlide formulation) have been subjected to tribological studies and comparison. Testing has been performed on the CSM pin/ball-on-disk tribometer. The Stribeck curve was chosen as a method to compare the performance of the oils. To generate the curve, several test stages were performed using the same sample and wear track. Each stage had a duration of five minutes at the following decreasing surface speeds then back up again: 12 cm/s, 10 cm/s, 8 cm/s, 4 cm/s, 2 cm/s, 1 cm/s, 0.5 cm/s , 0.25 cm/s, and 0.13 cm/s.

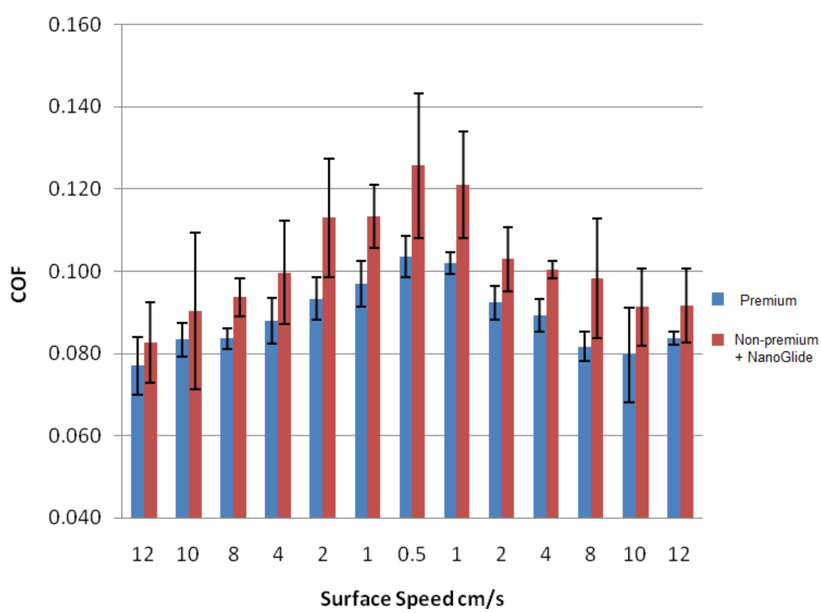

Figure 44. COF comparison of premium gear oil vs. non-premium gear oil with NanoGlide (initial formulation)

Figure 44 above, is based on three tests of both samples to show repeatability of the performance. For further comparison, the wear scar diameter of the ball was analyzed using a microscope. The results are shown in Figure 45.

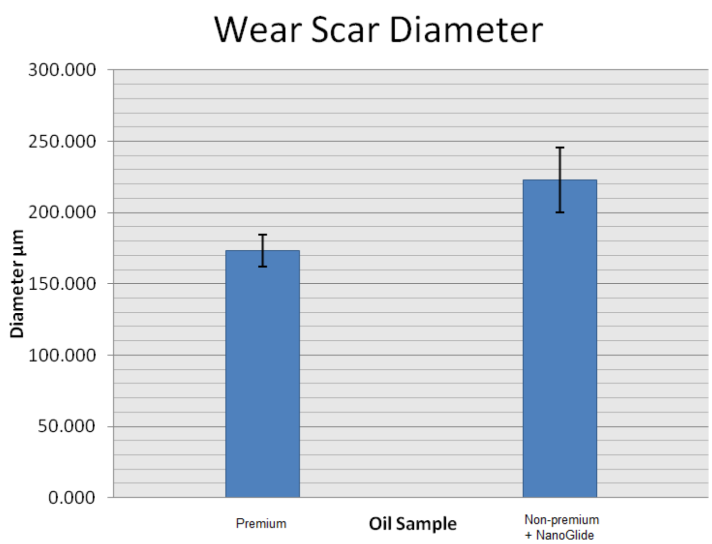

Figure 45. Wear scar diameter comparison of premium gear oil vs. non-premium gear oil with NanoGlide (initial formulation)

These results showed that the NanoGlide additive (initial formulation) in the non-premium oil did not outperform the premium gear oil. The new modified formulation of NanoGlide (described earlier in Task 4 of this report) will be used to improve the non-premium gear oil performance.

<u>Design of gear testing set-up for the study of lubricant performance</u>

For gear applications, the FZG test is the most effective large-scale test; the rig consists of a motor that drives two shafts through a slave gear box. One shaft has a torque measuring instrument and the other a loading clutch. These two shafts then input to the test gear box (Figure 46). The two standard tests for this rig are the scuffing test and the pitting test. The scuffing test uses profile A gear specimens and consists of incremental loading stages. The rpm is constant at 1400 rpm and run for 15 min at each stage with increasing load. When the wear scar on all teeth covers the tooth width the test is complete. The pitting test uses profile C gear specimens and is performed at a constant rpm and load until 4% of the tooth area is pitted [4].

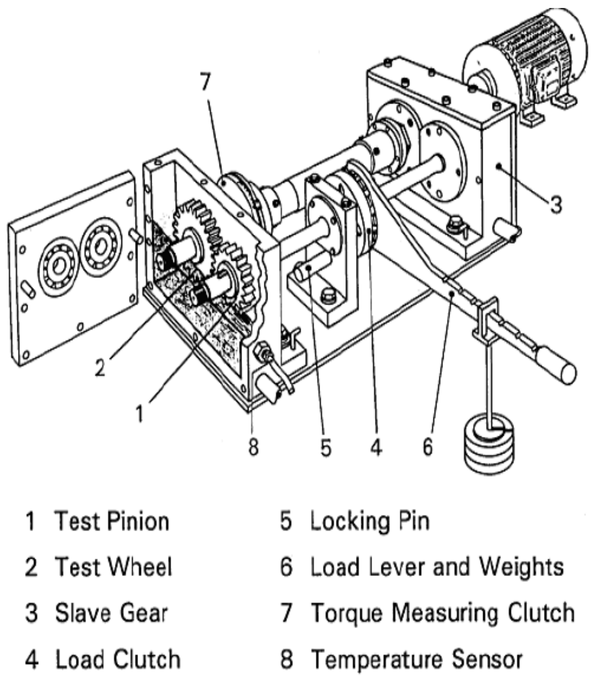

Figure 46. FZG test [4]

The FZG rig can also be used to measure the differences in power loss for different gear oil formulations. One method is to perform several no-load runs at different speeds, then several load runs at the same speeds. During those runs measurements of the motor torque and speed or electrical consumption of the motor can be taken to get the power loss comparison. The no-load runs will give the windage loss from the gears churning in the oil and the load runs will give the losses from the tooth interfaces.

Figure 47 shows the outline of the design described in this paragraph. A pulley system is used to convert the 1760 rpm of the motor to the required 1440 rpm of the test procedure. It is connected to the slave gears. Also, due to the tension of the pulleys this gearbox has a larger bending stress added to the shaft instead of mostly torsion stress. This increases the required shaft and bearing size for the gearbox. The gearbox is connected to the clutches using LoveJoy spider couplers to absorb any unwanted vibrations or slight misalignment. The system is mounted to a heavy cart for mobility but can be locked down during testing.

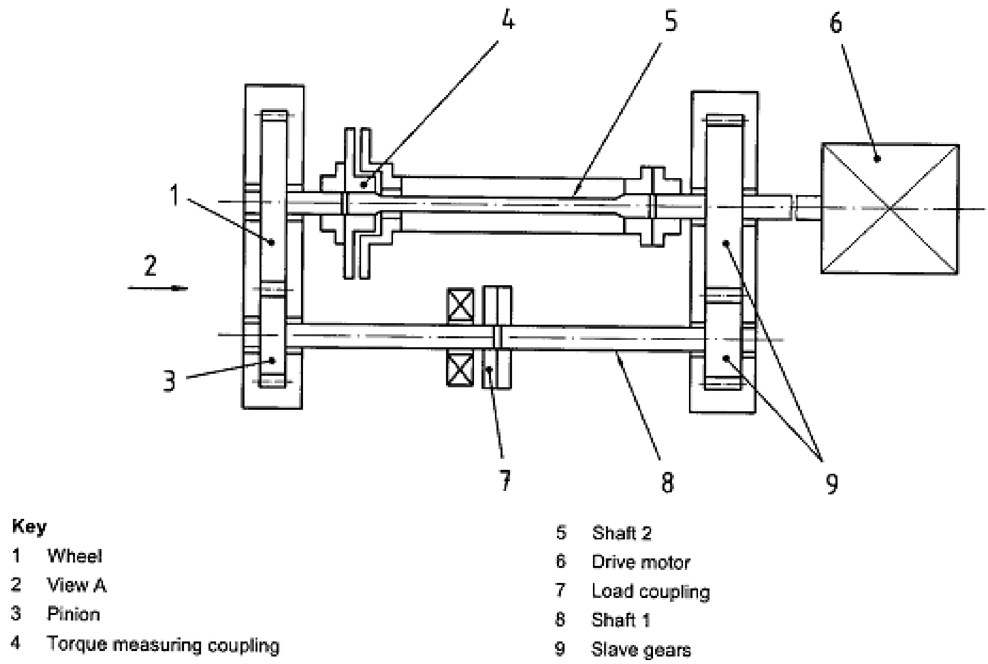

Figure 47. Schematic section of the FZG gear test machine [4]

In the previous reporting period, a parts list was developed for building the FZG rig. Purchasing of the required parts has been initiated, and the fabrication process has been started. The shaft and bearing requirements were calculated for achieving long service life given the motor output and required pinion torque.

In this reporting period, the design for the pulley system has been completed for transmitting the required power and torque. The proper gear set has also been sized to insure life expectancy of the test rig. The shaft design and bearing layout have been completed and sizing of the system for the required life span is in progress. The drive gear set is currently being quoted and the steel for the test rig cart is about to be ordered so welding can be started.

3D modeling for the test rig is underway and will be accompanied by a full set of engineering drawings for future use. The progress can be seen in Figures 48 and 49 below.

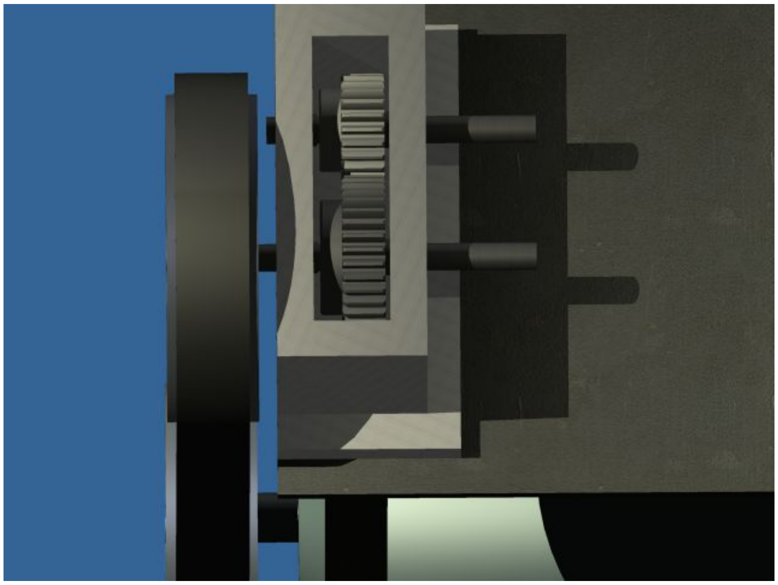

Figure 48. Drive gearbox layout

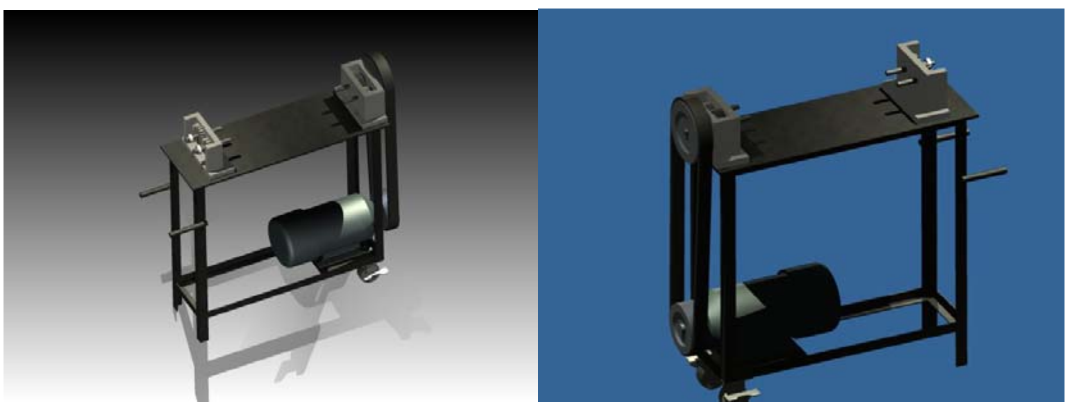

Figure 49. Test rig front (left) and back (right) view

Complementary analytical techniques will be used to fundamentally understand behavior of the NanoGlide unique chemistries in tribofilms. The investigation of nanolubricant behavior will involve chemical and structural analysis (XPS, SEM, and TEM) for understanding tribological behavior in Pin/Ball-on-Disk. The University of Arkansas is exploring an active partnership with a leading Tribology group at the Naval Research Laboratory (NRL). The University of Arkansas will collaborate, through exchange of student, with Dr. Kathryn J. Wahl (NRL) in using a specially designed instrument at NRL for *in situ* friction and wear analysis. This tribology approach will provide a more detailed understanding of the behavior of the nanolubricant at the nanoscale, directly at the point of loading contact, showing plastic behavior of the nanoparticles using an optically transparent pin/ball. A Raman signal tapped through the optically transparent pin/ball will carry the chemical signature of the event as it is occurring. This will give first-hand insight into the fundamental mechanism for behavior of the above novel chemistries.

Deliverables

Accomplished deliverables:

1. Design of experiments for tribological testing;
2. Tribological testing of NanoGlide samples in motor oils using 4 ball test, EP 4 ball test;
3. Tribological testing of NanoGlide samples in military oils using WAM test;
4. Design of FZG gear test machine;
5. Tribological testing of NanoGlide samples in motor and engine oils using pin/ball-on-disc, and engine oil using 4 ball test and EP 4 ball test.

Deliverables for 4th quarter of the project:

1. Tribological testing of NanoGlide using a test vehicle based on real gearbox housing (FZG test) [University of Arkansas];
2. Travel to NRL for studying *in situ* friction and wear behavior [University of Arkansas];
3. Understanding of nanolubricant behavior at the nanoscale loading contact;
4. Investigating the effects of nanolubricants addition into regular military gear oil and their tribological performance using WAM test.

Task 6: Commercialization of NanoGlide

Navy oil and greases

The Navy specifies and procures oils and greases for many different applications. For shipboard use, the Naval Ships' Technical Manual (S9086-H7-STM-010/CH-262R4) Chapter 262, "Lubricating Oils, Greases, Specialty Lubricants, and Lubrication Systems" provides information regarding the various lubricants and their applications. Individual military specifications provide requirements for specific lubricants.

The group within the Navy that is responsible for lubricants used in ships is NAVSEA Code 05P25, which is a part of the Naval Sea Systems Command located in Washington, DC. For shipboard use, the Navy has not made significant changes in lubricants or lubricant requirements for some time. Shipboard applications identified that could be explored for potential nanolubricant application include the following:

1. Main reduction gears. This appears to be a good candidate as it is a major gearing system that operates under heavy load. 2190 TEP lube oil (further discussion below) is used in some reduction gears.

2. Controllable pitch propellers. The pitch control is a hydraulic application with bearing surfaces that see high loads.

3. Other hydraulic systems that are highly loaded; such as steering gears, aircraft arresting gears, and possibly elevator lift mechanisms.

2190 TEP is a turbine lube oil that is used as the lube oil of first choice for shipboard propulsion plant applications (reduction gears, steam turbines, and more). The Navy's desire is to have a single lube oil that is used in propulsion plants to simplify logistic support and crew operations (reduces the chance of using the wrong lube oil, simplifies carrying spare oil, etc.). However, a problem has been experienced with the 2190 oil "coking" on the surface of electric lube oil heaters. Also, we understand that the Navy is having trouble finding vendors willing to continue making 2190 to Navy specs and has given vendors some waivers to change additives. The Navy, however, is concerned about the long term effects on equipment, sailors, environment, etc. of these additives that have not had experience in the Navy environment. These are important items to consider as NanoGlide is developed and validated for Navy shipboard applications.

In addition to ships, helicopters also have lubricant applications that could be addressed by NanoGlide. For example, helicopter drive trains and gearboxes are limited in the amount of power that they can deliver, due in part to limitations of the lubricants used. If a new lubricant can reduce friction, this will increase the power transmitted by the drive train. NanoGlide is being evaluated through gear simulation tests using WAM test rigs, which are commonly used to validate performance of lubricants for helicopters and other aerospace applications.

Commercialization updates

We have been actively engaging blenders of oils and greases, as well as oil and grease users and suppliers. We have also been talking to Navy program managers for an SBR under the JSF program and Air Force MANTECH SBIR program.

NanoMech will use compatible oil as a milling material to form as an initial product a concentrate, which contains approximately 50% by weight of the solid NanoGlide. This can be added directly to grease at the 5% level or blended into oils at the 1% to 2% level. When supplying to oil formulators, it will be advantageous to pre-dilute the concentrate in the oil of their choice as formulators typically do not have dispersion capability. Scale up plans have been outlined and it has been verified that scaled-up costs will be competitive.

The first premium market for NanoGlide will include military and civilian areas where there are real technical issues, such as extreme pressure wear (wind turbines); wear, friction and temperature (Joint Strike Fighter), and extreme pressure / coefficient of friction (auto and bike racing). Products for these applications can command premium pricing and we are working with formulators and customers in these markets.

The second premium market is the retail consumer market where performance additive quantities are small and margins are large throughout the value chain. Representative materials have been acquired and are being benchmarked. One of our partners has expressed interest in entering this market with us.

The third premium sector is OEM oils. These are specified by truck makers or bearing makers as a condition of extended warranties. Sealed-for-life and pre-lubed bearings are examples of this and there is an aftermarket for branded oils and greases. We plan to engage members of the DoE Vehicle Technology program and other programs to ensure our products are evaluated for reduced energy consumption.

One customer perception challenge with NanoGlide is the color – black, like all molybdenum disulfides. Engine oil is perceived as clean by consumers when it is amber, dirty when it is black. Consumers however almost never see gear oil or other oils or greases. Transport lubricants are changed per schedule, not by color. Industrial greases come in a number of colors and for most applications black is not a problem except in applications when fresh grease is pumped into a filled joint and filling is complete when the fresh grease color is identified at the bleed nipple. Other areas of concern are food processing where white or green greases are used. We are addressing this issue by identifying color-sensitive market niches and testing alternatives to molybdenum disulfides with a white appearance, such as boron nitride and other boron compounds. Because nanomaterials are smaller than the wavelength of light, the opacity of the NanoGlide materials will be relatively low and so the addition of a pigment, dye, or other tracing material in fresh grease would be quite practical.

In summary we have identified that:

1. The product can be scaled economically;
2. Premium and commodity markets exist;
3. There are no insurmountable barriers to entering these markets;
4. There are receptive partners who will enable us to enter these markets.

<u>Regulatory and Environmental Update</u>

We have carried out an initial life cycle assessment for the NanoGlide products and have not found any major issues in production of the raw materials, manufacturing, oil use, oil recycling, or grease disposal (grease is not normally recycled but is usually incinerated). The production itself is low energy and potentially very high yield with no by-product streams. Lowered coefficients of friction and improved extreme pressure performance will make a significant contribution to reliability and energy conservation in transportation and major industrial markets including wind energy generation.

We are assessing the acute toxicity of the product during a new Department of Energy Phase 2 SBIR (DE-SC0003593) which is anticipated to start in November 2010. We have identified and had initial contacts with experts in Washington who have experience in dealing with EPA and FDA (food contact lubricant) issues and can advise us of any current or upcoming registration requirements.

We foresee the opportunity to use NanoGlide products as a replacement for ZDDP, the most popular extreme-pressure lubricant, which is being withdrawn from the engine oil market because of its deleterious effect on exhaust catalysts.

Conclusions

NanoGlide lubricants address the diverse application needs of the Navy, including lower coefficient of friction, smaller wear scar, high loading capability, good strength of tribofilm and equally important, little or no time to respond to “dry and harsh” conditions and deliver a tribofilm as a result of plastic deformation, when trapped among asperities. Target applications expected to be of interest to the Navy, for on- and off- shore purposes, are bearings, gear boxes, and engines.

In the third quarter of this project, the initial two formulations of NanoGlide were modified to specifically address their application as additives in gear oils and greases. These improved formulations were investigated using chemical, structural, and tribological analysis. A Design of Experiments (DoE) approach for synthesis and optimization using a scaled-up production process was applied to analyze interactions among process parameters and to select optimal synthesis parameters to be used with optimal process time.

Tribological testing of NanoGlide® additives in gear oils using Pin-on-Disk test and Block-on-Ring test, and in greases using 4 Ball test and EP 4 Ball test was performed, and evolution and comparison of their performance is presented and discussed in this report. The FZG gear test rig is being prepared and is on schedule.

This project has revealed several advantages of having NanoGlide® in lubricant formulations (gear oils and greases). It provides advanced lubrication for severe friction conditions (extreme pressure and loads) by extending component life and lube-drain intervals in comparison to base oils and greases. It is a technology that could increase the efficiency and durability of machinery components, particularly gears, leading to longer operation intervals and lower maintenance costs. Another beneficial feature is that it is non-disruptive and insertable into current lubricant production processes, and there is a wide range of industrial applications in which it can be put to use.

The scaled-up process was developed and process parameters were optimized. Morphological and tribological properties of samples from the scaled-up production were compared with properties of samples from laboratory-scale production. The outcomes of this comparison show similar particle size distribution and level of agglomeration of nanoparticles for both processes and shortened process time for the scaled-up process, thus contributing to the technical objective of extended shelf life and suspension stability of nanoparticle additives, and the commercial goal of increasing yield per batch with significant reduction in processing time.

The lubrication testing of modified formulations of NanoGlide® in military oils will be completed using the WAM test in the next quarter and tested using the developed gear testing set up (FZG test).

Cost and financial status

	Budget	Actual Q1	Actual Q2	Actual Q3	Total
NanoMech, Inc.	$707,727	$77,374	$110,288	$307,874	$495,536
University of Arkansas (subcontract)	$61,261	$0	$0	$34,034	$34,034
Total costs	$768,988	$77,374	$110,288	$341,908	$529,570

References

1. Malshe, A., Verma, A. (January 2006), Nanoparticles Based Lubricants, Patent Pending.
2. Malshe, A., Verma, A. (July 2006), Active Nanoparticles: Synthesis, Behavior And Applications, Patent Pending.
3. Komvopoulos, K., Pernama, S.A.; Ma, J.; Yamaguchi, E.S.; Ryason, P.R. (2005), Synergistic Effects of Boron-, Sulfur-, And Phosphorus-Containing Lubricants in Boundary Lubrication of Steel Surfaces Tribology Transactions, 48 (2), 218.
4. ISO 14635-1, FZG test method A/8,3/90 for relative scuffing load carrying capacity of oils.

Publications and presentations:

Article entitled “Advanced Nanolubricant Additives” was submitted to Compoundings Magazine of the Independent Lubricant Manufacturers Association (ILMA).

Appendix A: Project Plan Timeline

Table A1. Technical Tasks

	Tasks	MONTH 1-2	MONTH 3-4	MONTH 5-6	MONTH 7-8	MONTH 9-10	MONTH 11-12
1.	***Designing of application-specific active nanolubricant (NanoGlide)***						
2.	***Process scale up and nanomanufacturing NanoGlide***						
3.	***Synthesis, de-agglomeration and optimization of NanoGlide***						
4.	***Structural, chemical, and physical analysis of NanoGlide***						
5.	***Tribological testing of NanoGlide***						
6.	***Commercialization of NanoGlide***						